Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Hydrosilylative Reduction of Secondary Amides to Amines Catalyzed by Geometric-Constrained NNN-Cobalt Complexes

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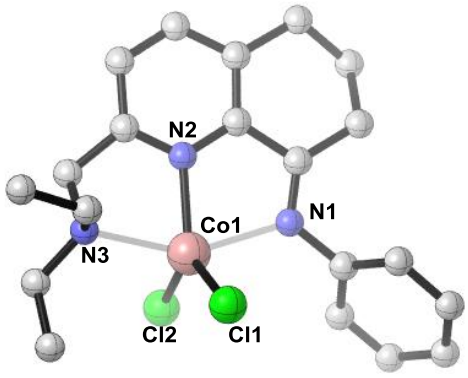
1. X-ray analysis of Co-3



Co-3

Figure S1. Solid structure of complex **Co-3**. Hydrogen atoms were emitted for clarity.

Table S1. Crystal data and structure refinement for Complex **Co-3.**

Identification code	a_a	
Empirical formula	$C_{20}H_{25}Cl_2CoN_3$	
Formula weight	437.26	
Temperature	193(2) K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.1324(3) Å	α= 90 °.
	b = 11.1382(3) Å	β= 90 °.
	c = 16.7579(5) Å	γ = 90 °.
Volume	2077.89(10) $Å^3$	
Z	4	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	6.145 mm^{-1}	
F(000)	908	
Crystal size	0.180 x 0.160 x 0.160 mm^3	
Theta range for data collection	4.146 to 53.950 °.	
Index ranges	-13<=h<=13, -13<=k<=13, -20<=l<=20	
Reflections collected	25981	
Independent reflections	3799 [R(int) = 0.0623]	
Completeness to theta = 53.594 °	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	

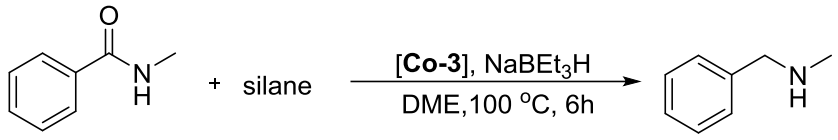
Data / restraints / parameters	3799 / 0 / 238
Goodness-of-fit on F^2	0.913
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0660
R indices (all data)	R1 = 0.0362, wR2 = 0.0688
Absolute structure parameter	0.030(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.264 and -0.247 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [°] for **Ni1**.

selected bond lengths [Å]		selected angles [°]	
Co(1)−Cl(1)	2.2644(10)	N(2)-Co(1)-N(1)	74.83(11)
Co(1)−Cl(2)	2.2673(11)	N(2)-Co(1)-Cl(1)	126.94(9)
Co(1)−N(1)	2.241(3)	N(1)-Co(1)-Cl(1)	90.34(8)
Co(1)−N(2)	2.030(3)	N(2)-Co(1)-Cl(2)	110.22(9)
Co(1)−N(3)	2.281(3)	N(1)-Co(1)-Cl(2)	100.16(8)
		Cl(1)-Co(1)-Cl(2)	122.58(4)
		N(2)-Co(1)-N(3)	77.74(12)
		N(1)-Co(1)-N(3)	151.42(11)
		Cl(1)-Co(1)-N(3)	99.82(8)
		Cl(2)-Co(1)-N(3)	96.69(9)

2. Optimizations for Co-catalyzed hydrosilylative reduction of amide.

Table S3. The effects of various silanes.

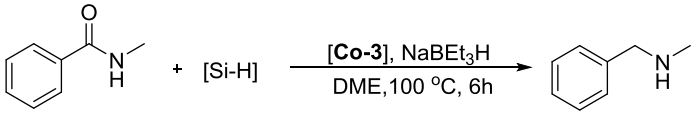


1a **2a**

Entry	Silane	Conv. (%)	Yield (%)[b]
1	$PhSiH_3$	100	80
2	Ph_2SiH_2	55	52
3	Et_3SiH	n.r.	0
4	$(EtO)_3SiH$	16	12
5	$(MeO)_3SiH$	n.r.	0

[a] Reaction conditions: **1a** (1.0 mmol), silane (3.0 mmol), cat (2 mol%), $NaBEt_3H$ (10 mol%), Solvent (2 mL) at 100 °C, 6 h. [b] Conversions were obtained with GC area normalization. [c] Yields were obtained with GC analysis using biphenyl as an internal standard.

Table S4. The effects of temperature, catalyst loading, the reaction time, and the amount of PMHS



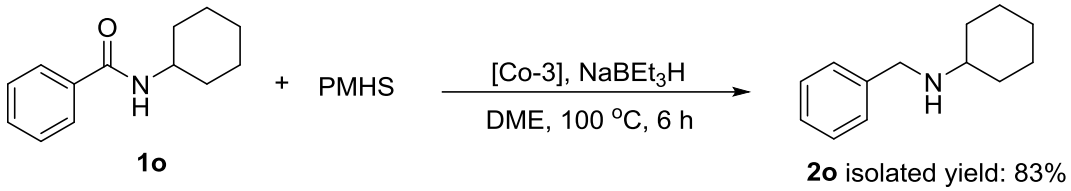
1a **2a**

Entry	Temp. (°C)	**Cat.** (mol%)	Time (h)	[Si-H] (eq.)	Yield (%)[b]
1	80	**Co-3** (2)	6	10	73
2	90	**Co-3** (2)	6	10	81
3	100	**Co-3** (2)	6	10	89
4	110	**Co-3** (2)	6	10	84
5	120	**Co-3** (2)	6	10	76
6	100	**Co-3** (1)	6	10	77
7	100	**Co-3** (2)	6	10	87
8	100	**Co-3** (3)	6	10	90
9	100	**Co-3** (4)	6	10	91
10	100	**Co-3** (5)	6	10	93

11	100	**Co-3** (2)	4	10	48
12	100	**Co-3** (2)	5	10	67
13	100	**Co-3** (2)	6	10	85
14	100	**Co-3** (2)	7	10	82
15	100	**Co-3** (2)	8	10	70
16	100	**Co-3** (2)	6	3	36
17	100	**Co-3** (2)	6	6	46

[a] Reaction conditions: **1a** (1.0 mmol), PMHS (3-10 mmol Si-H), cat (1-5mol%), $NaBEt_3H$ (10 mol%), Solvent (2 mL) at 80-120 °C, 4-8 h. [b] Yields were obtained with GC analysis using biphenyl as an internal standard.

3. Procedure for gram scale reaction

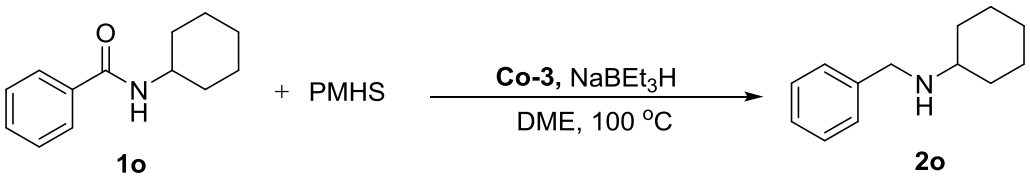


1o **2o** isolated yield: 83%

To a Young tube, was charged with **Co-3** (44 mg, 0.1 mmol), **1o** (1.0 g, 5 mmol), PMHS (3.4 mL), DME (10.0 mL) and $NaHBEt_3$ (0.5 mL, 0.5 mmol). The mixture was stirred at 100 °C for 6 h, the reaction temperature was allowed to cool to room temperature. The reaction was diluted with DCM, and then aqueous sodium hydroxide was added and stirred at room temperature for 1 h. After extraction and concentration, The residue was then purified by flash column chromatography using petroleum ether as eluent to afford **2o** (784 mg, 83%) as a yellow oil.

4. Kinetic experiments.

4.1 Kinetic investigation for the reduction of 1o



1o **2o**

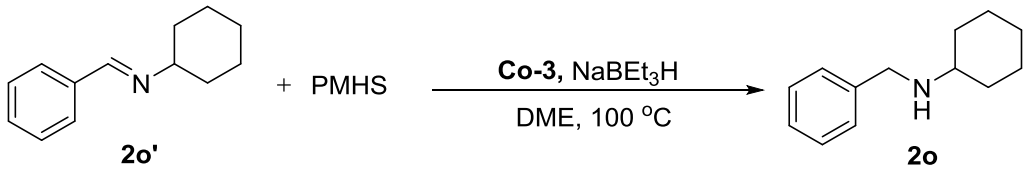
To a Young tube was charged with **Co-3** (4.4 mg, 0.01 mmol), **1o** (102 mg, 0.5 mmol), PMHS (340 μL), DME (1.0 mL) and $NaHBEt_3$ (50 μL, 0.05 mmol). The mixture was stirred at 100 °C for the designed reaction time (see Tab S3). Then,

the reaction temperature was allowed to cool to room temperature. The reaction was diluted with DCM, and then aqueous sodium hydroxide was added and stirred at room temperature for 1 h. The amount of **1o** and **2o** were obtained with n-dodecane as the internal standard as shown in the table below.

Table S5. Kinetic data for the reduction of **1o**.

Entry	Time/min	**1o** (mmol)	**2o** (mmol)
1	0	0.5	0
2	60	0.315	0.077
3	120	0.185	0.155
4	180	0.125	0.240
5	240	0.1	0.310
6	300	0.035	0.4
7	360	0.035	0.430

4.2 Kinetic investigation for the reduction of 2o'



To a Young tube was charged with **Co-3** (4.4 mg, 0.01 mmol), **2o'** (94 mg, 0.5 mmol), PMHS (340 μL), DME (1.0 mL) and $NaHBEt_3$ (50 μL, 0.05 mmol). The mixture was stirred at 100 °C for the designed reaction time (see Tab S6). Then, the reaction temperature was allowed to cool to room temperature. The reaction was diluted with DCM, and then aqueous sodium hydroxide was added and stirred at room temperature for 1 h. The amount of **2o'** and **2o** were obtained with n-dodecane as the internal standard as shown in the table below

Table S6. Kinetic data for for the reduction of **2o'**.

Entry	Time/min	**2o'** (mmol)	**2o** (mmol)
1	0	0.5	0

2	5	0.380	0.110
3	10	0.260	0.220
4	25	0.150	0.325
5	35	0.060	0.410
6	75	0.015	0.450
7	120	0.010	0.455
8	240	0.005	0.460
9	360	0.005	0.460

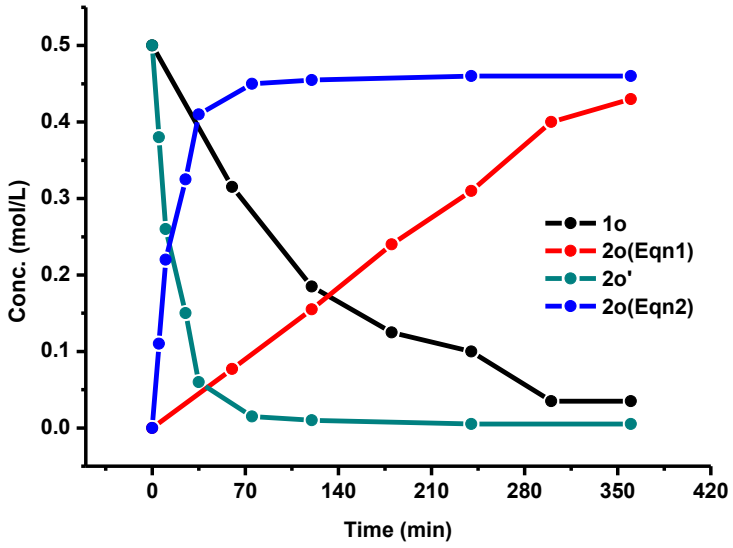
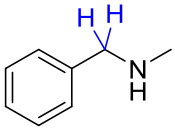
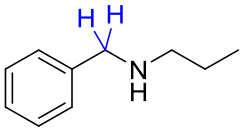


Figure S2. Kinetic diagram for the reduction of **2o** and **2o'**

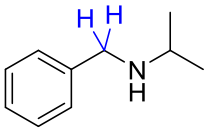
5. Spectra of products



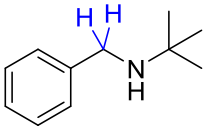
***N*-methyl-1-phenylmethanamine (2a)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (131 mg, 88% yield). ^{1}H NMR (600 MHz, DMSO-d6) δ7.38 – 7.26 (m, 4H), 7.22 (t, *J* = 6.8 Hz, 1H), 3.64 (s, 2H), 2.67 (s, 2H). ^{13}C NMR (150 MHz, DMSO-d6) δ 141.3, 128.5, 128.3, 126.9, 55.7, 36.1.



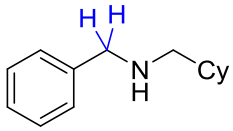
***N*-benzylpropan-1-amine (2b)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (131 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 7.29-7.23 (m, 1H), 3.81 (s, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 1.60 – 1.50 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 128.4, 128.1, 126.8, 54.0, 51.4, 23.2, 11.8.



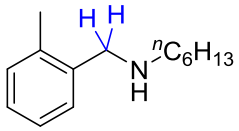
***N*-benzylpropan-2-amine (2c)[2]**: The title compound was purified by column chromatography (PE:EA=1:1) to afford the product as a colorless oil (113 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 3.80 (s, 2H), 2.88 (sep, *J* = 6.2 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 129.1, 128.4, 128.1, 126.8, 51.6, 48.1, 22.9.



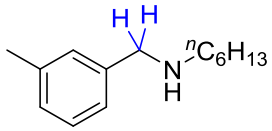
***N*-benzyl-2-methylpropan-2-amine (2d)[3]**: The title compound was purified by column chromatography (PE:EA=1:1) to afford the product as a colorless oil (144 mg, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (d, J = 7.6 Hz, 2H), 7.31-7.26 (m, 2H), 7.20 (t, J = 7.4 Hz, 1H), 3.65 (s, 2H), 1.10 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 142.6, 129.1, 128.4, 126.7, 50.6, 46.8, 29.4.



***N*-benzyl-1-cyclohexylmethanamine (2e)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (161 mg, 79% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34–7.26 (m, 4H), 7.19 (t, J = 7.0 Hz, 1H), 3.66 (s, 2H), 2.30 (d, J = 6.6 Hz, 2H), 1.77–1.69 (m, 2H), 1.68–1.57 (m, 3H), 1.43–1.31 (m, 1H), 1.25–1.07 (m, 3H), 0.89–0.79 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 141.7, 128.4, 128.2, 126.8, 56.0, 53.7, 38.1, 31.6, 26.8, 26.1.

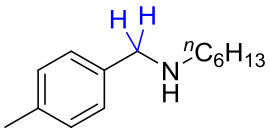


***N*-(2-methylbenzyl)hexan-1-amine (2f)[4]**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (160 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29–7.25 (m, 1H), 7.13–7.09 (m, 3H), 3.63 (s, 2H), 2.51 (t, J = 7.4 Hz, 2H), 2.27 (s, 3H), 1.47–1.39 (m, 2H), 1.33–1.18 (m, 6H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.9, 135.9, 129.7, 128.1, 126.3, 125.4, 50.9, 49.2, 31.3, 29.5, 26.6, 22.1, 18.5, 13.9.

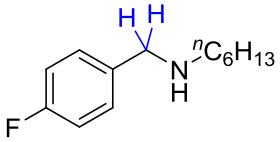


***N*-(3-methylbenzyl)hexan-1-amine (2g)[5]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (168 mg, 82% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.17 (t, J = 7.6 Hz, 1H), 7.12 (s, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 3.62 (s, 2H), 2.45 (t, J = 7.3

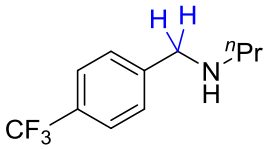
Hz, 2H), 2.28 (s, 3H), 1.44–1.35 (m, 2H), 1.31-1.16 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 140.9, 137.0, 128.5, 127.9, 127.0, 124.9, 53.0, 48.7, 31.3, 29.4, 26.5, 22.1, 21.0, 13.9.



***N*-(4-methylbenzyl)hexan-1-amine (2h)[5]**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a colorless oil (164 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.18 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.62 (s, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.27 (s, 3H), 1.43–1.37 (m, 2H), 1.29–1.21 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.5, 135.7, 129.0, 128.2, 53.3, 49.1, 31.8, 30.0, 27.0, 22.6, 21.1, 14.4.

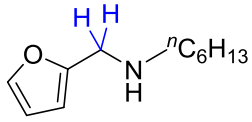


***N*-(4-fluorobenzyl)hexan-1-amine (2i)[5]**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a pale yellow oil (209 mg, 84% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 – 7.31 (m, 2H), 7.10 – 7.06 (m, 2H), 3.63 (s, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.40 – 1.38 (m, 2H), 1.27 – 1.20 (m, 6H), 0.85 – 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.5 (d, *J* = 241.4 Hz), 137.7 (d, *J* = 2.9 Hz), 130.0 (d, *J* = 8.1 Hz), 115.1 (d, *J* = 21.7 Hz), 52.7, 49.1, 31.8, 30.0, 27.0, 22.6, 14.3.

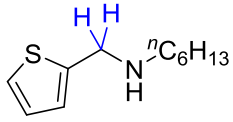


***N*-(4-(trifluoromethyl)benzyl)propan-1-amine (2j)[6]**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (191 mg, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 3.75 (s, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.49–1.36

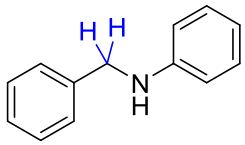
(m, 2H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 146.7, 128.9, 127.6 (q, J = 31.7 Hz), 125.3 (q, J = 3.6 Hz), 124.9 (q, J = 281.7 Hz, 1C), 52.9, 51.1, 23.1, 12.2.



***N*-(furan-2-ylmethyl)hexan-1-amine (2k)[8]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (152 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, J = 1.8, 0.7 Hz, 1H), 6.29 (dd, J = 3.1, 1.8 Hz, 1H), 6.16 (d, J = 3.3 Hz, 1H), 3.76 (s, 2H), 2.58 (t, J = 7.3 Hz, 2H), 1.58-1.40 (m, 2H), 1.37–1.19 (m, 6H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 141.6, 110.0, 106.6, 49.2, 46.3, 31.7, 30.0, 27.0, 22.6, 14.0.

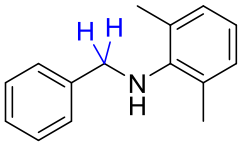


***N*-(thiophen-2-ylmethyl)hexan-1-amine (2l)[8]**: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (160 mg, 81% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.33 (dd, J = 4.7, 1.6 Hz, 1H), 6.95-6.90 (m, 2H), 3.85 (s, 2H), 2.49 (t, J = 7.2 Hz, 2H), 1.46–1.34 (m, 2H), 1.30–1.16 (m, 6H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ145.4, 126.4, 124.2, 124.2, 48.5, 47.8, 31.2, 29.4, 26.5, 22.1, 13.9.

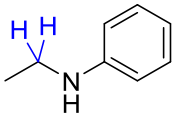


***N*-benzylaniline (2m)[6]**: The title compound was purified by column chromatography (PE:EA=5:1) to afford the product as a colorless oil (157 mg, 86% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37 (d, J = 7.3 Hz, 2H), 7.34-7.29 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.08-7.00 (m, 2H), 6.59 (d, J = 8.3 Hz, 2H), 6.52 (t, J = 7.3, 1H), 6.22 (t, J = 5.7 Hz, 1H), 4.27 (d, J = 6.0 Hz, 2H). ^{13}C NMR

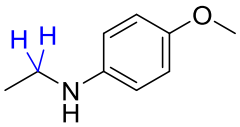
(125 MHz, DMSO-d_6) δ 149.2, 140.8, 129.3, 128.7, 127.6, 127.0, 116.2, 112.8, 47.0.



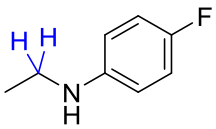
***N*-benzyl-2,6-dimethylaniline (2n)[9]**: The title compound was purified by column chromatography (PE:EA=50:1) to afford the product as a colorless oil (114 mg, 54% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26– 7.20 (m, 1H), 6.91 (d, *J*=7.6 Hz, 2H), 6.72 (t, *J*=7.6 Hz, 1H), 4.09 (s, 2H), 2.20 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 146.3, 141.4, 129.8, 128.9, 128.6, 128.2, 127.2, 121.7, 51.8, 18.9.



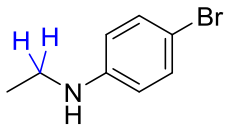
***N*-ethylaniline (4a)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (104 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19–7.13 (m, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.45 (br, 1H), 3.12 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 38.5, 15.0.



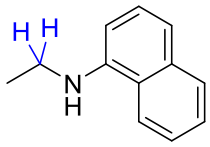
***N*-ethyl-4-methoxyaniline (4b)[1]**: The title compound was purified by column chromatography (PE:EA=5:1) to afford the product as a colorless oil (137 mg, 91% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.71 (d, *J* = 8.8 Hz, 2H), 6.53–6.51 (d, *J* = 8.8 Hz, 2H), 4.99 (br, 1H), 3.63 (s, 3H), 2.96 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 151.1, 143.8, 115.0, 113.5, 55.8, 38.6, 15.0.



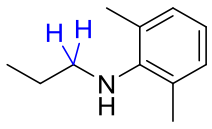
***N*-ethyl-4-fluoroaniline (4c)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (114 mg, 82% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.89 (t, J = 8.8 Hz, 2H), 6.52 (dd, J = 8.8, 4.6 Hz, 2H), 5.39 (br, 1H), 2.97 (q, J = 7.3 Hz, 2H), 1.14 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 154.5 (d, J = 230.8 Hz, 1C), 146.2, 115.6 (d, J = 22.2 Hz, 2C), 113.1 (d, J = 7.5 Hz, 2C), 38.3, 14.8.



4-bromo-N-ethylaniline (4d)[1]: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (141 mg, 71% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.18 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 8.7 Hz, 2H), 5.73 (t, J = 4.7 Hz, 1H), 2.98 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 148.6, 131.8, 114.2, 106.4, 37.7, 14.7.

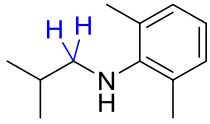


***N*-ethylnaphthalen-1-amine (4e)[10]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (154 mg, 90% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 8.1 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 6.04 (br, 1H), 3.22 (q, J = 6.5 Hz, 2H), 1.29 (t, J = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 144.6, 134.5, 128.4, 127.3, 126.0, 124.3, 123.5, 122.2, 115.7, 103.3, 38.1, 14.6.

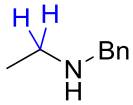


2,6-dimethyl-N-propylaniline (4f)[11]: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (101 mg, 62% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.91 (d, J = 7.5 Hz, 2H), 6.70 (t, J

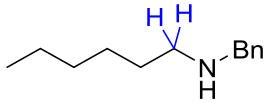
= 7.5 Hz, 1H), 2,86 (t, *J* = 7.6 Hz, 2H), 2.21 (s, 6H),1.54 – 1.44 (m, 2H), 0.9 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 146.9, 129.3, 128.9, 121.3, 50.1, 24.1, 18.9, 12.0.



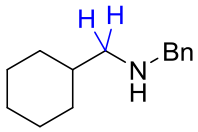
N-isobutyl-2,6-dimethylaniline (4g)[12]: The title compound was purified by column chromatography (PE) to afford the product as a pale yellow oil (106 mg, 60% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.91 (d, *J* = 7.4 Hz, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 3.61 (br, 1H), 2.71 (d, *J* = 6.6 Hz, 2H), 2.22 (s, 6H), 1.79 – 1.71 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 146.9, 129.3, 128.9, 121.3, 56.1, 29.4, 20.8, 18.8.



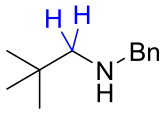
***N*-benzylethanamine (4h)[11]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (110 mg, 82% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.26-7.21 (m,1H), 3.78 (s, 2H), 2.67 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.6, 128.4, 128.2, 126.9, 54.0, 43.7, 15.3.



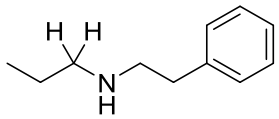
***N*-benzylhexan-1-amine (4i)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (158 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4H), 7.26–7.22 (m, 1H), 3.78 (s, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.55-1.45 (m, 2H), 1.35–1.23 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.6, 128.5, 128.2, 127.0, 54.2, 49.6, 31.9, 30.2, 27.2, 22.8, 14.2.



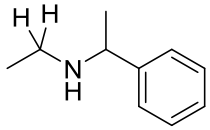
***N*-benzyl-1-cyclohexylmethanamine (4j)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (102 mg, 85% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34–7.26 (m, 4H), 7.23–7.17 (m, 1H), 3.67 (s, 2H), 2.31 (d, J = 6.6 Hz, 2H), 1.78–1.70 (m, 2H), 1.68–1.57 (m, 3H), 1.42–1.32 (m, 1H), 1.24–1.08 (m, 3H), 0.89–0.79 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 141.7, 128.4, 128.2, 126.8, 56.0, 53.7, 38.1, 31.6, 26.8, 26.1.



***N*-benzyl-2,2-dimethylpropan-1-amine (4k)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (134 mg, 76% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36–7.25 (m, 4H), 7.24-7.16 (m, 1H), 3.70 (s, 2H), 2.20 (s, 2H), 0.86 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.8, 128.5, 128.2, 126.8, 61.4, 54.3, 31.9, 28.2.

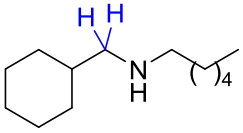


***N*-phenethylpropan-1-amine (4l)[13]**: The title compound was purified by column chromatography (PE:EA=5:1) to afford the product as a pale yellow oil (148 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.22–7.19 (m, 3H), 2.87 (t, J = 7.3 Hz, 2H), 2.81 (t, J = 7.3 Hz, 2H), 2.58 (t, J = 7.3 Hz, 2H), 1.53-1.43 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.2, 128.8, 128.6, 126.2, 51.8, 51.2, 36.5, 23.2, 11.8.

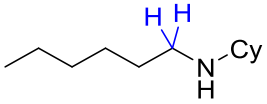


***N*-ethyl-1-phenylethan-1-amine (4m)[14]**: The title compound was purified by column chromatography (PE:EA=30:1) to afford the product as a yellow oil (119 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34–7.23 (m, 4H), 7.22-7.14 (m, 1H), 3.66 (q, J = 7.1 Hz, 1H), 2.39–2.24 (m, 2H), 1.21 (d, J = 6.6 Hz, 3H),

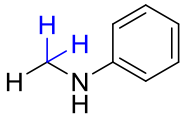
0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 146.9, 128.6, 126.9, 126.8, 58.0, 41.8, 25.0, 15.6.



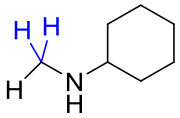
***N*-(cyclohexylmethyl)hexan-1-amine (4n)[15]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (185 mg, 94% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.43 (t, *J* = 7.0 Hz, 2H), 2.30 (d, *J* = 6.6 Hz, 2H), 1.73–1.58 (m, 5H), 1.39–1.10 (m, 15H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.9, 50.2, 38.1, 31.8, 31.6, 30.1, 27.0, 26.8, 26.1, 22.6, 14.4.



***N*-hexylcyclohexanamine (4o)[2]**: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (144 mg, 79% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.48 (t, *J* = 6.9 Hz, 2H), 2.33–2.26 (m, 1H), 1.82–1.73 (m, 2H), 1.67–1.61 (m, 2H), 1.56–1.50 (m, 1H), 1.37–1.32 (m, 2H), 1.29–1.10 (m, 10H), 1.00–0.92 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 56.7, 46.9, 33.5, 31.8, 30.5, 27.1, 26.4, 24.9, 22.6, 14.4.

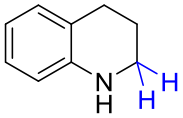


***N*-methylaniline (4p)[1]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (92 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 3.71 (br, 1H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 129.3, 117.3, 112.5, 30.8.

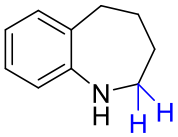


***N*-methylcyclohexanamine (4q)[16]**: The title compound was purified by column chromatography (PE) to afford the product as a yellow oil (101 mg, 90% yield).

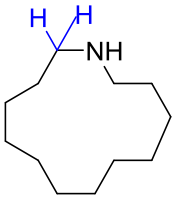
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H),2.30 – 2.23 (m, 1H), 1.87 – 1.83 (m, 2H), 1.71 – 1.67 (m, 2H), 1.60 – 1.55 (m, 1H), 1.29 – 1.09 (m, 3H), 1.04 – 0.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 58.5, 33.6, 33.2, 26.2, 25.0.



1,2,3,4-tetrahydroquinoline (6b)[17]: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (106 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.85-6.77 (m, 2H), 6.46–6.34 (m, 2H), 5.59 (br, 1H), 3.16 (t, *J* = 5.5 Hz, 2H), 2.64 (t, *J* = 6.3 Hz, 2H), 1.82–1.73 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.8, 129.4, 126.8, 120.3, 115.5, 113.8, 41.3, 27.2, 22.0.



2,3,4,5-tetrahydro-1H-benzo[b]azepine (6d)[18]: The title compound was purified by column chromatography (PE) to afford the product as a colorless oil (117 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.00 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 5.16 (br, 1H), 2.89 (t, *J* = 4.5 Hz, 2H), 2.65-2.60 (m, 2H), 1.72–1.61 (m, 2H), 1.58–1.49 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 151.3, 132.2, 130.3, 126.2, 119.3, 118.9, 47.6, 35.4, 31.5, 26.7.



Azacyclotridecane(6e)[10]: The title compound was purified by column chromatography (EA) to afford the product as a yellow solid (150 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (t, *J* = 6.5 Hz, 4H), 1.77-1.58 (m, 4H), 1.51-1.16 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.1, 25.5, 25.3, 25.1, 24.1, 23.5.

N-methyl-1-phenylmethanamine (2a)

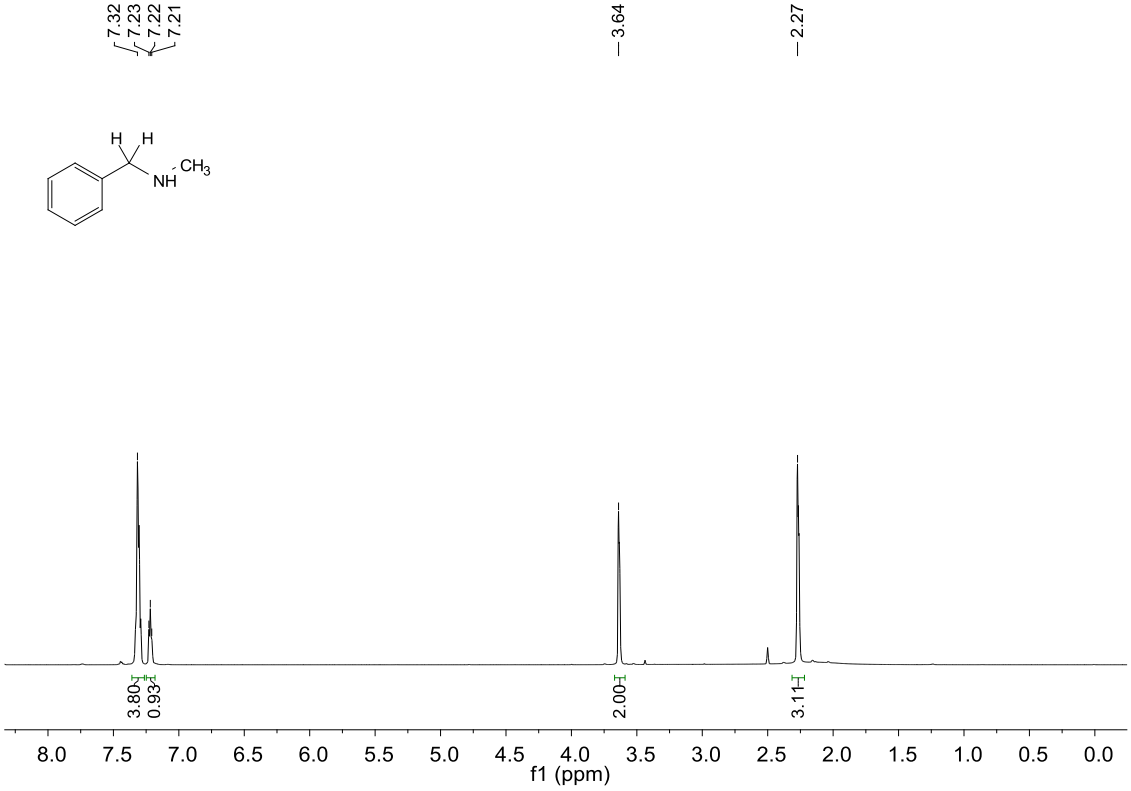


Figure S3. ^{1}H NMR (600 MHz) spectrum of **2a** in $CDCl_3$

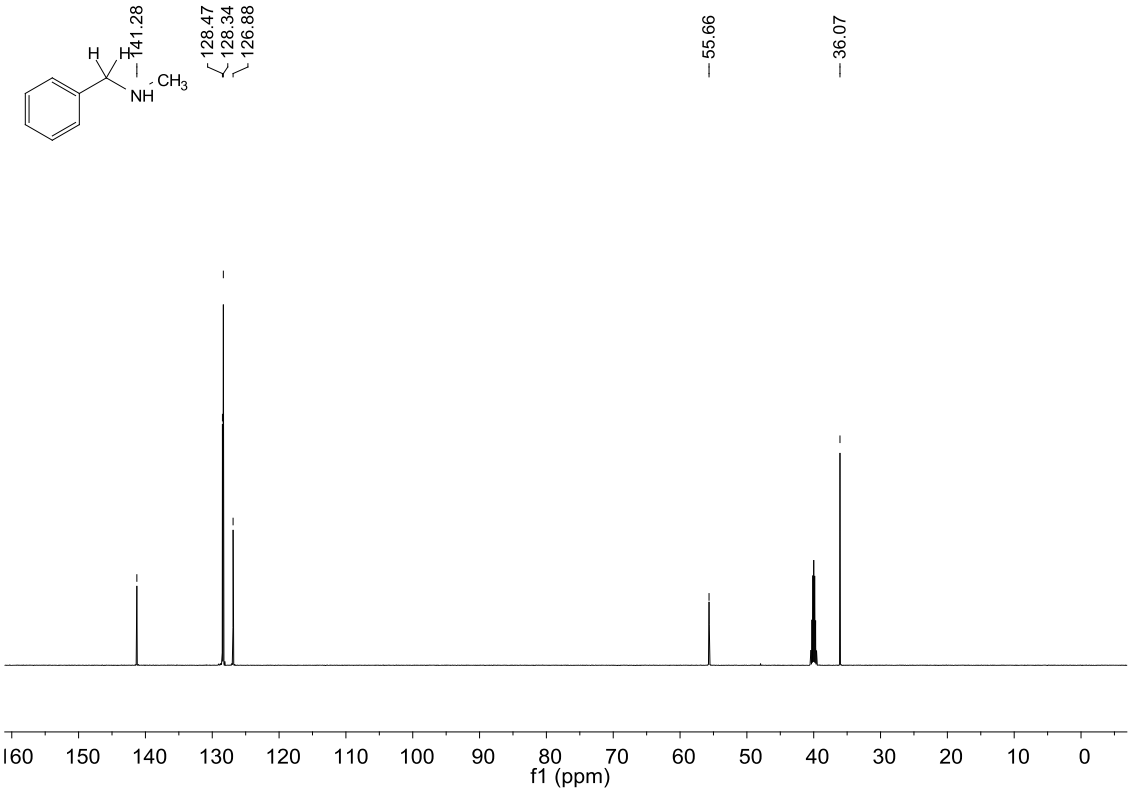


Figure S4. ^{13}C NMR (150 MHz) spectrum of **2a** in $CDCl_3$

N-benzylpropan-1-amine (2b)

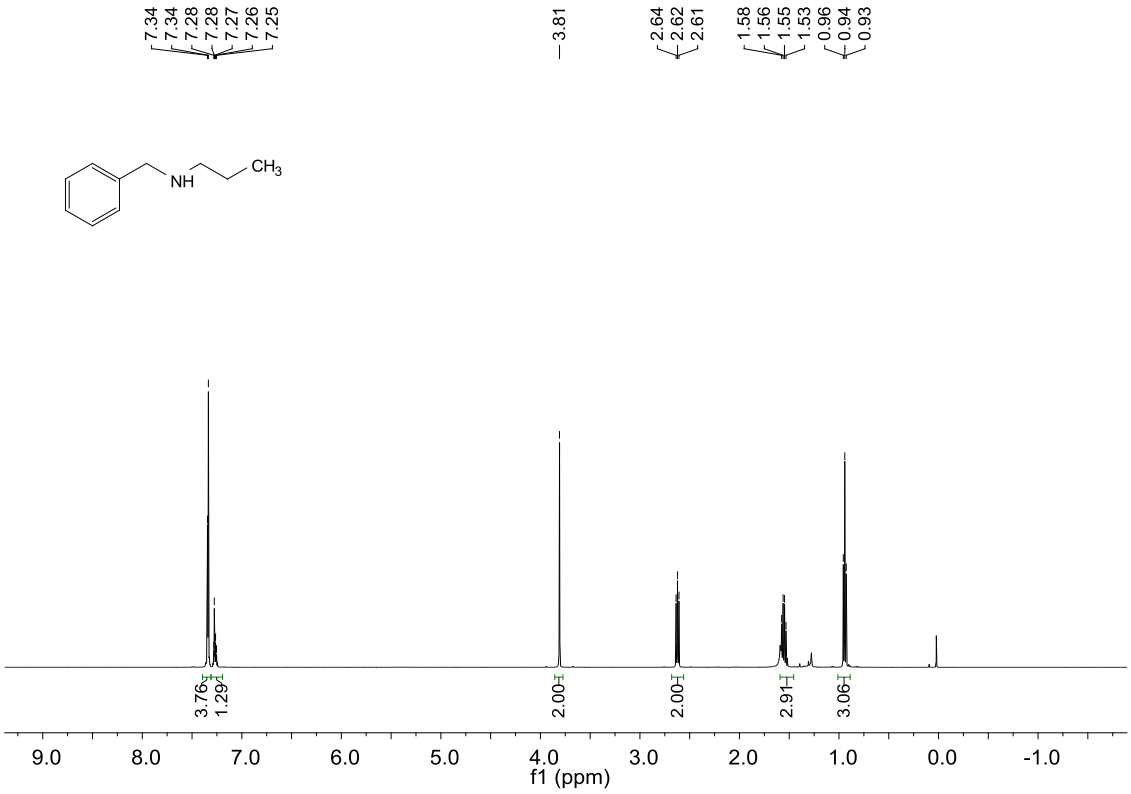


Figure S5. ^{1}H NMR (500 MHz) spectrum of **2b** in $CDCl_3$

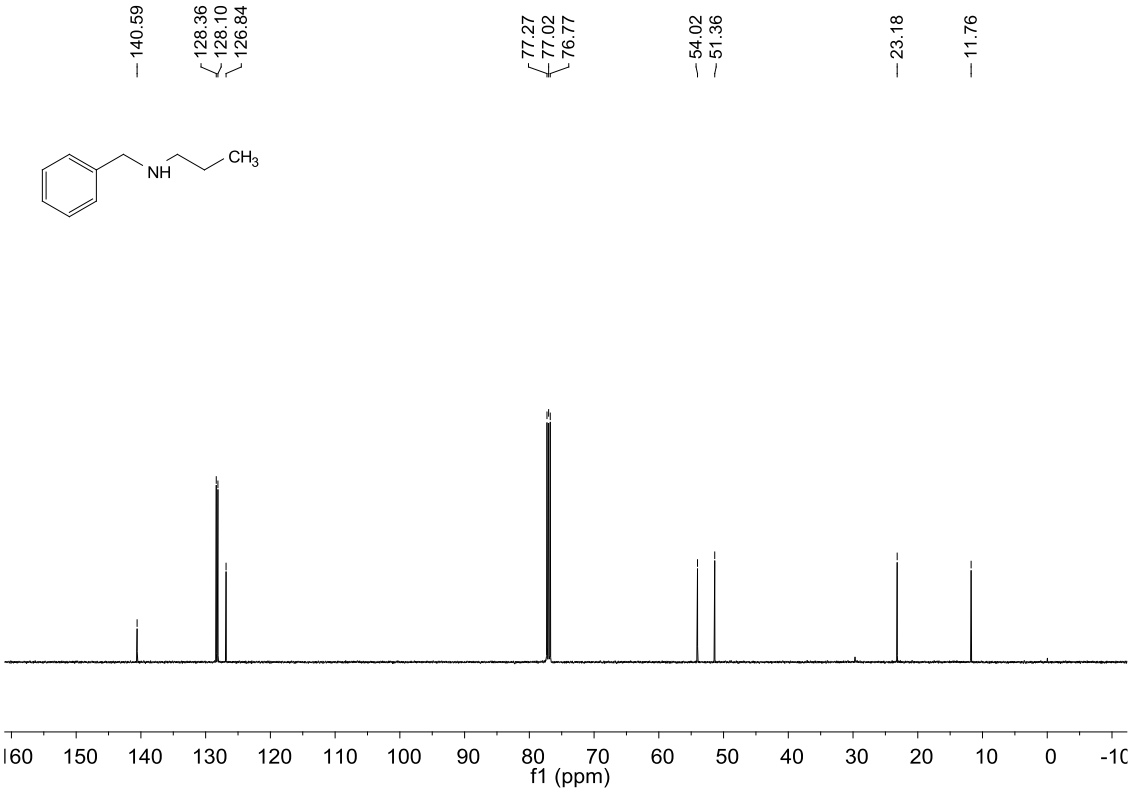


Figure S6. ^{13}C NMR (125 MHz) spectrum of **2b** in $CDCl_3$

N-benzylpropan-2-amine (2c)

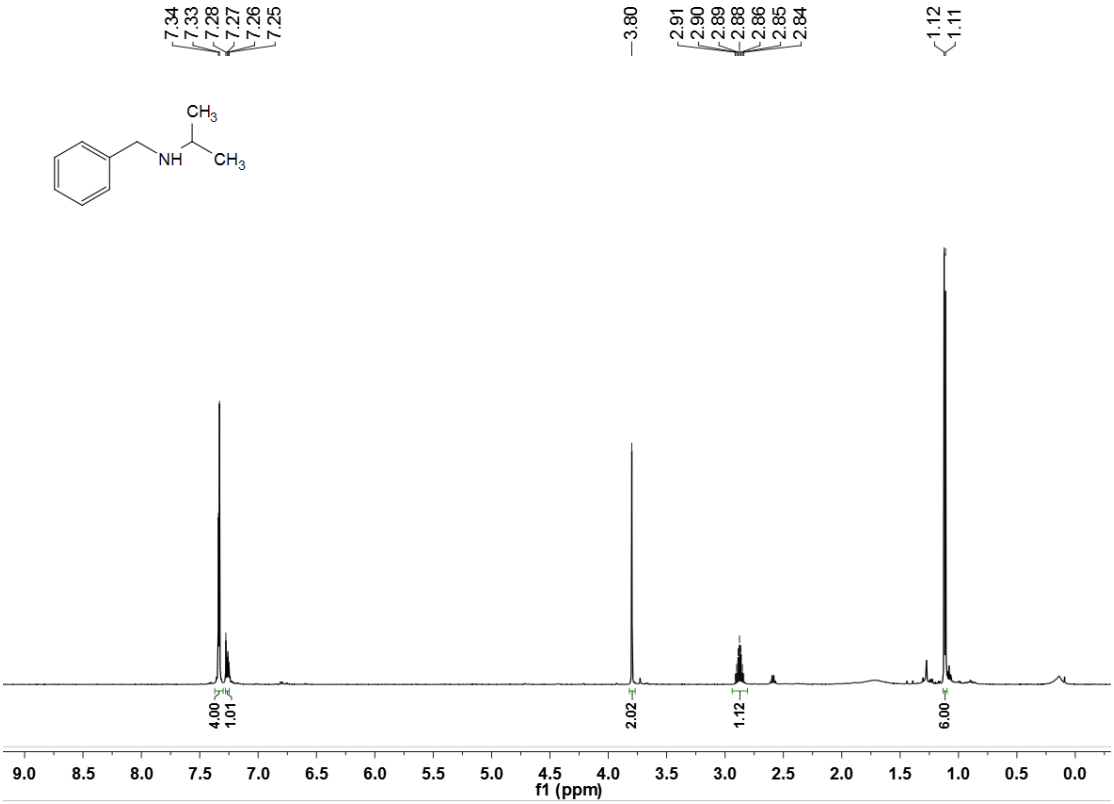


Figure S7. ^{1}H NMR (500 MHz) spectrum of **2c** in $CDCl_3$

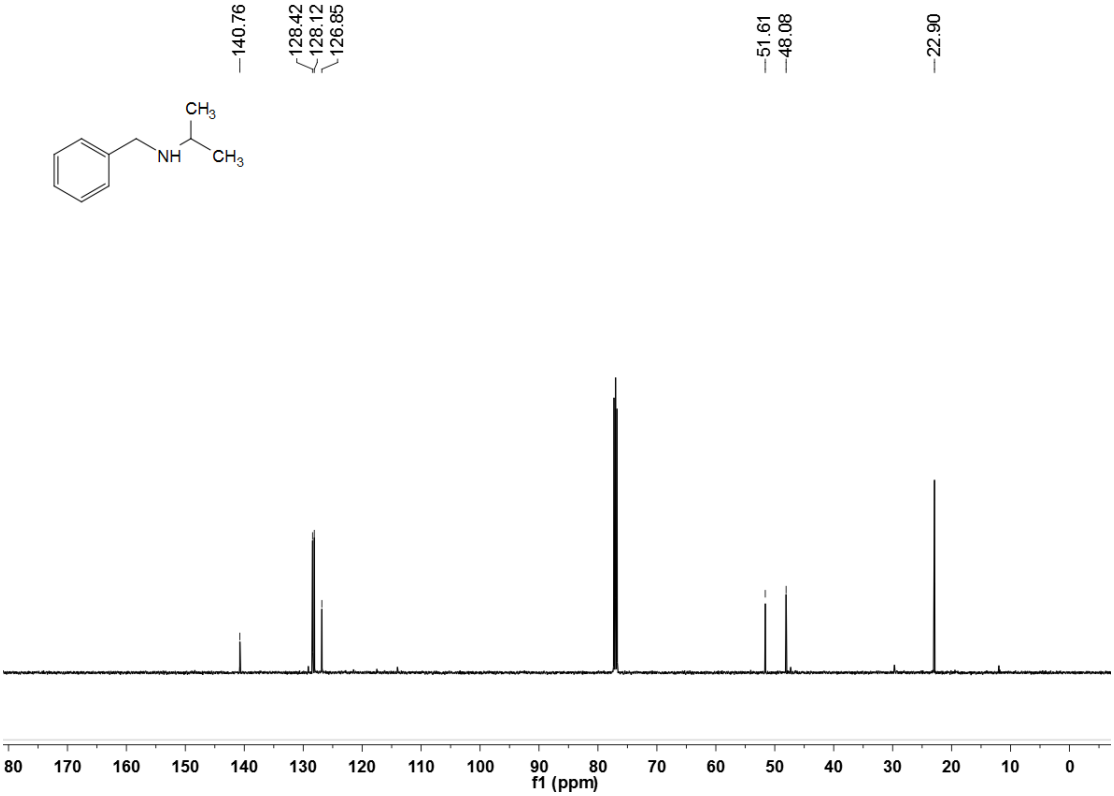


Figure S8. ^{13}C NMR (125 MHz) spectrum of **2c** in $CDCl_3$

N-benzyl-2-methylpropan-2-amine (2d)

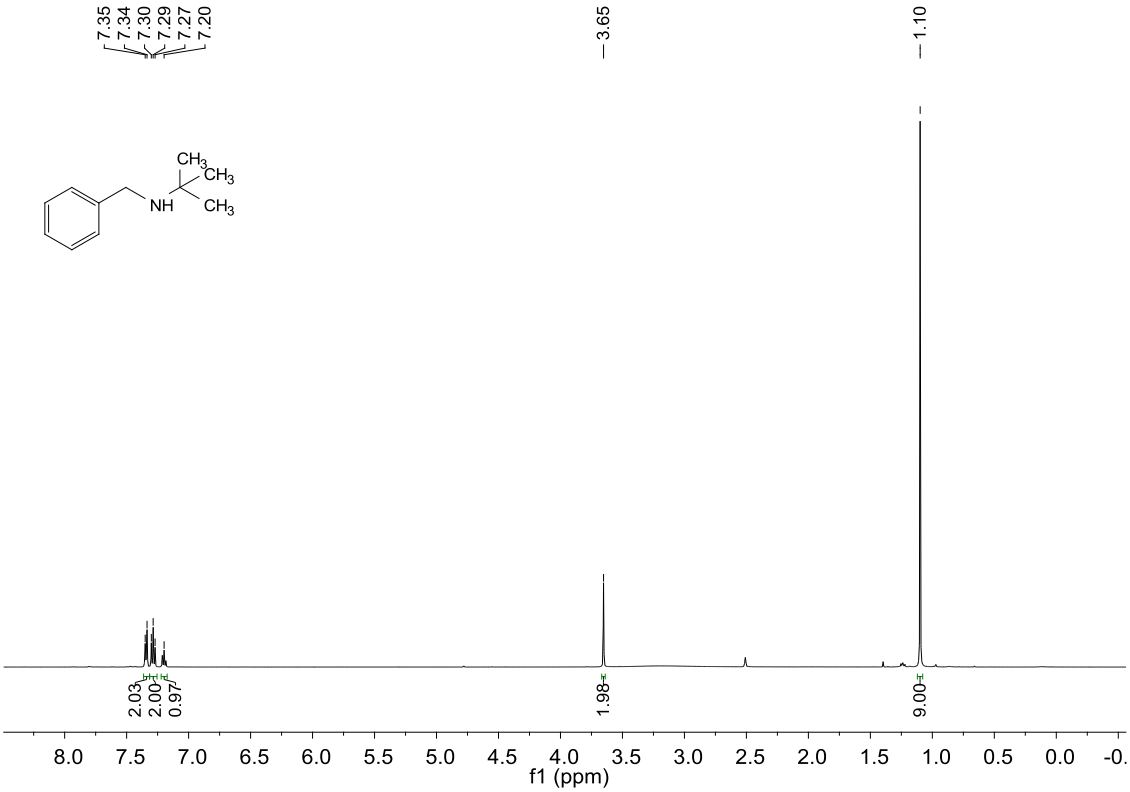


Figure S9. ^{1}H NMR (500 MHz) spectrum of **2d** in DMSO-*d*6

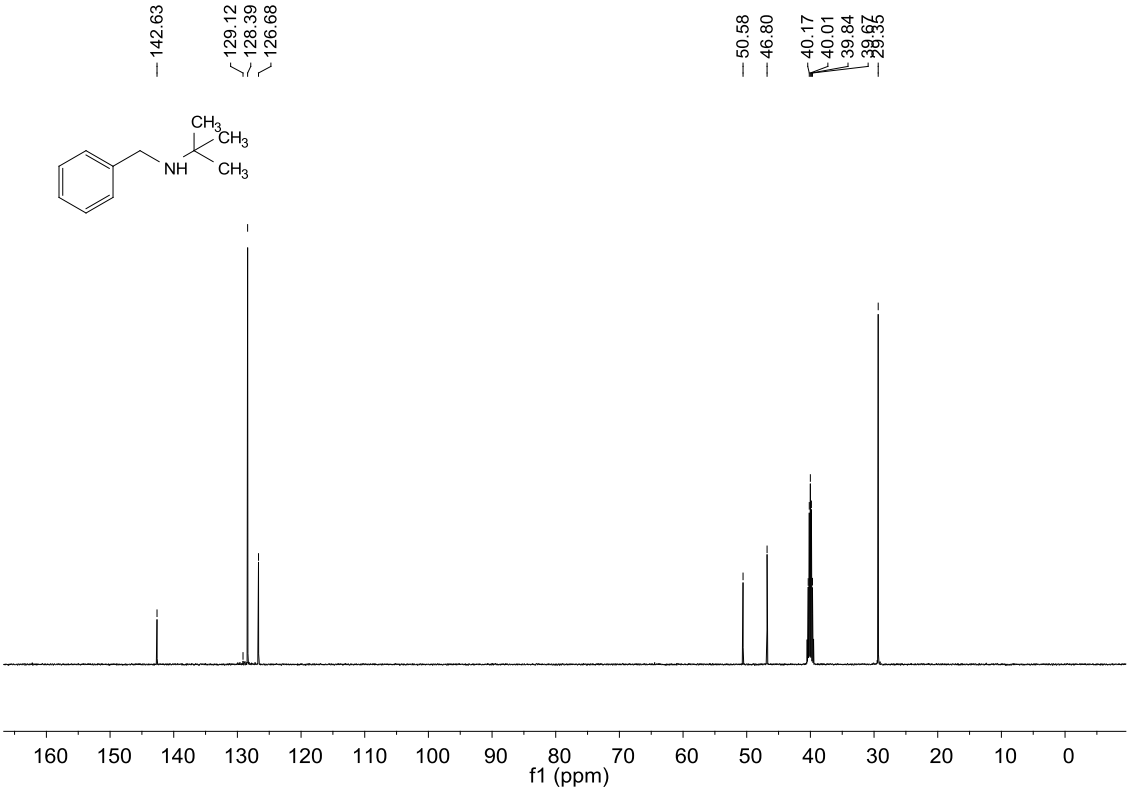


Figure S10. ^{13}C NMR (125 MHz) spectrum of **2d** in DMSO-*d*6

N-benzyl-1-cyclohexylmethanamine (2e)

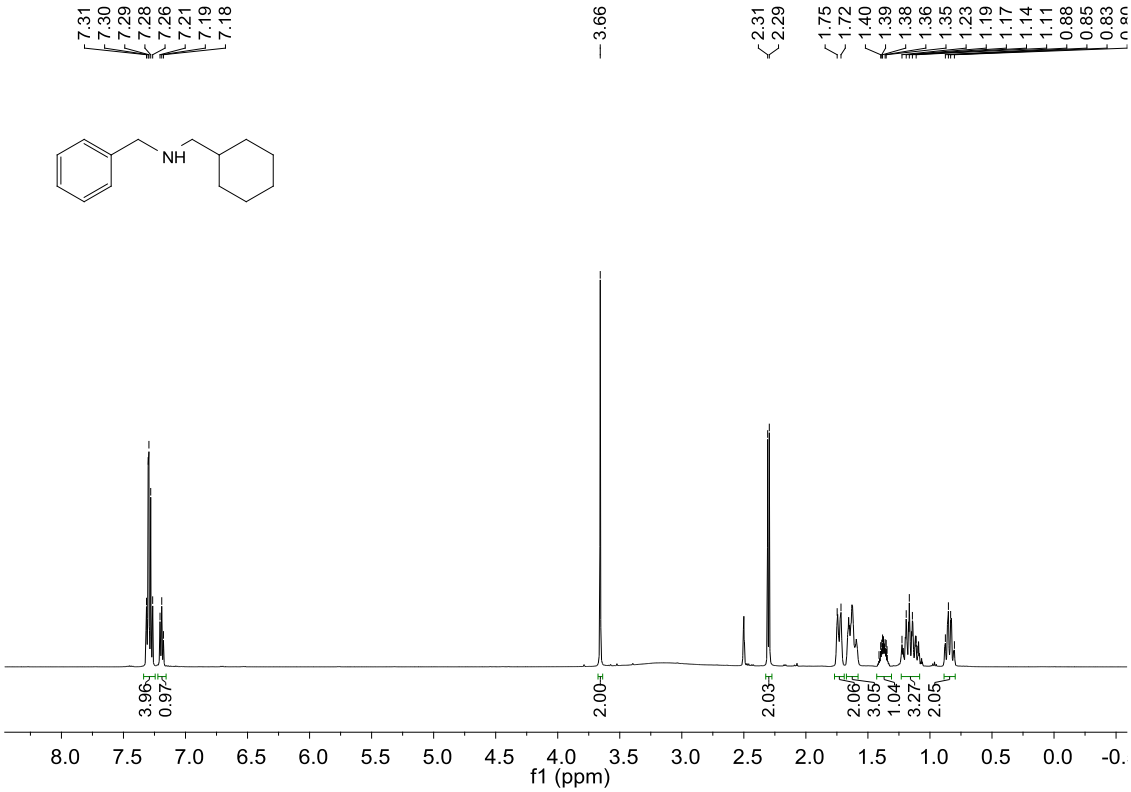


Figure S11. [1]H NMR (500 MHz) spectrum of **2e** in DMSO-*d*6

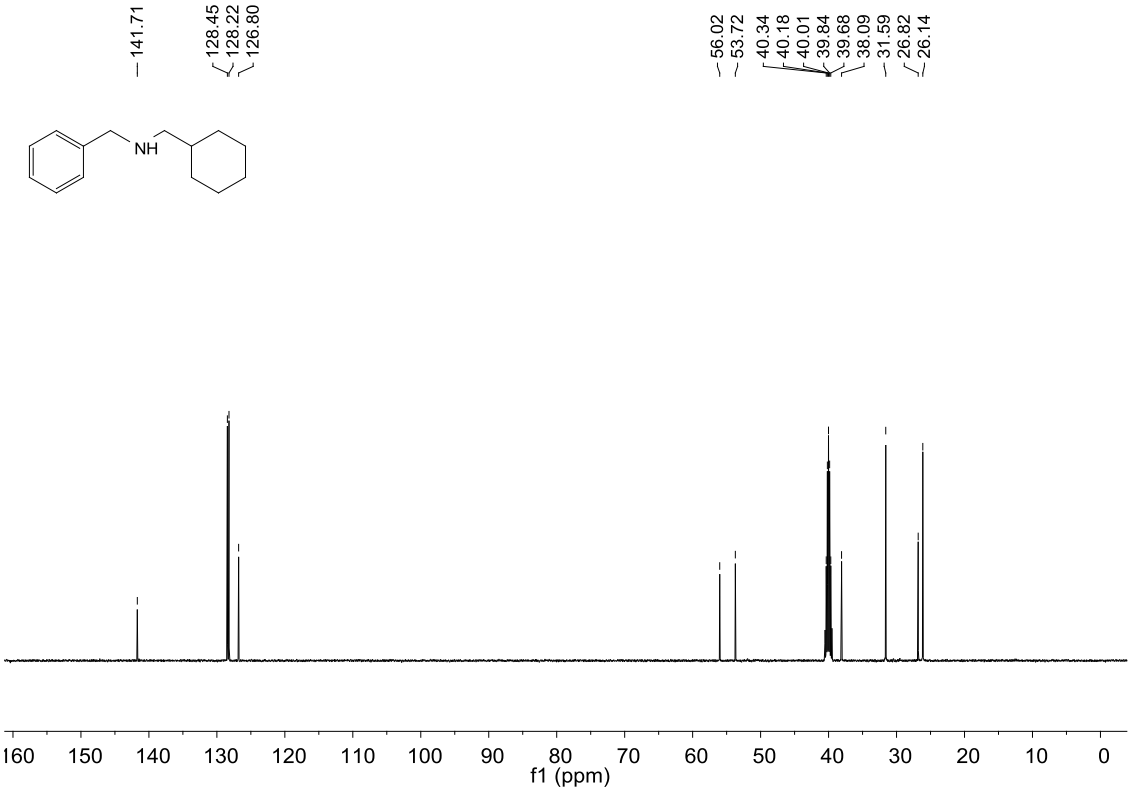


Figure S12. [13]C NMR (125 MHz) spectrum of **2ed** in DMSO-*d*6

N-(2-methylbenzyl)hexan-1-amine (2f)

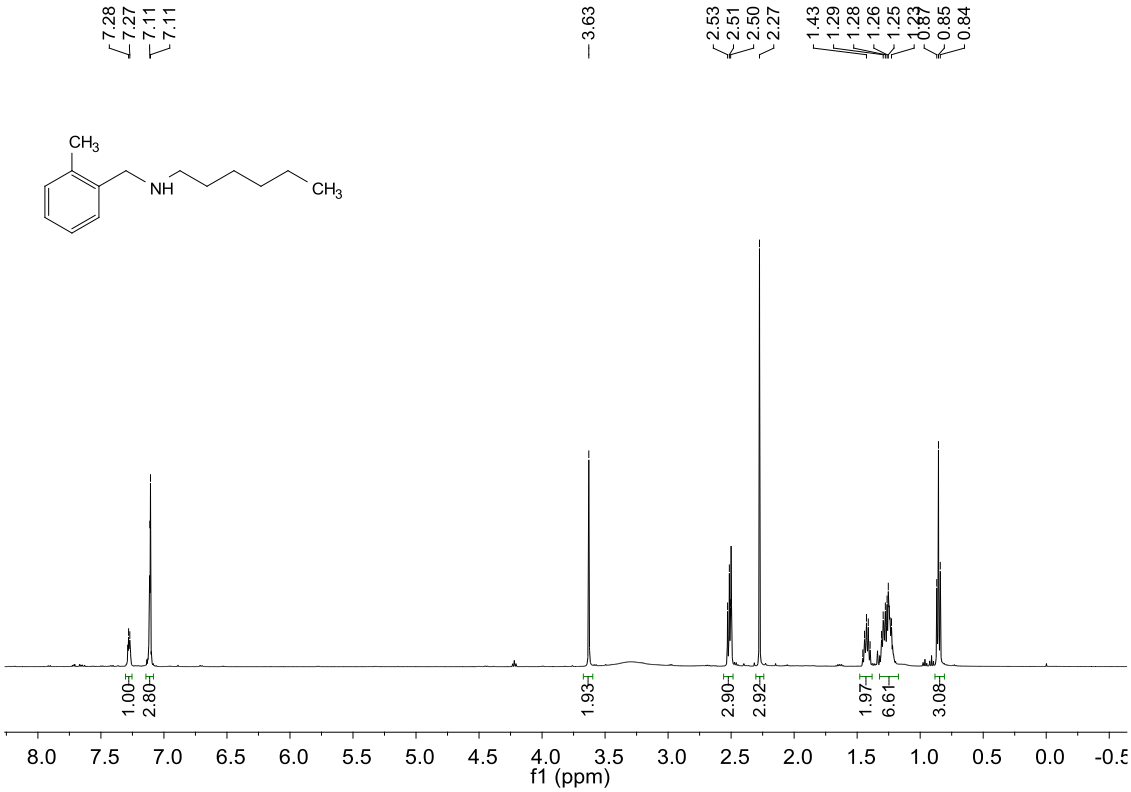


Figure S13. ^{1}H NMR (500 MHz) spectrum of **2f** in DMSO-*d*6

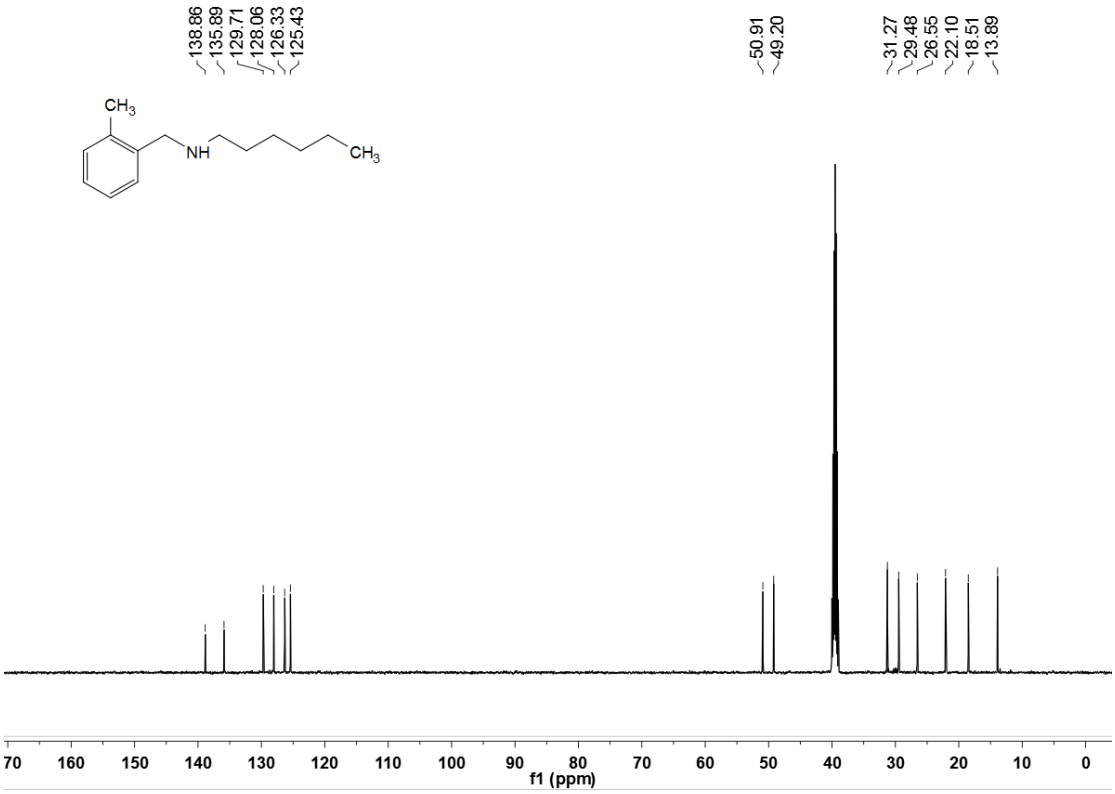


Figure S14. ^{13}C NMR (125 MHz) spectrum of **2f** in DMSO-*d*6

N-(3-methylbenzyl)hexan-1-amine (2g)

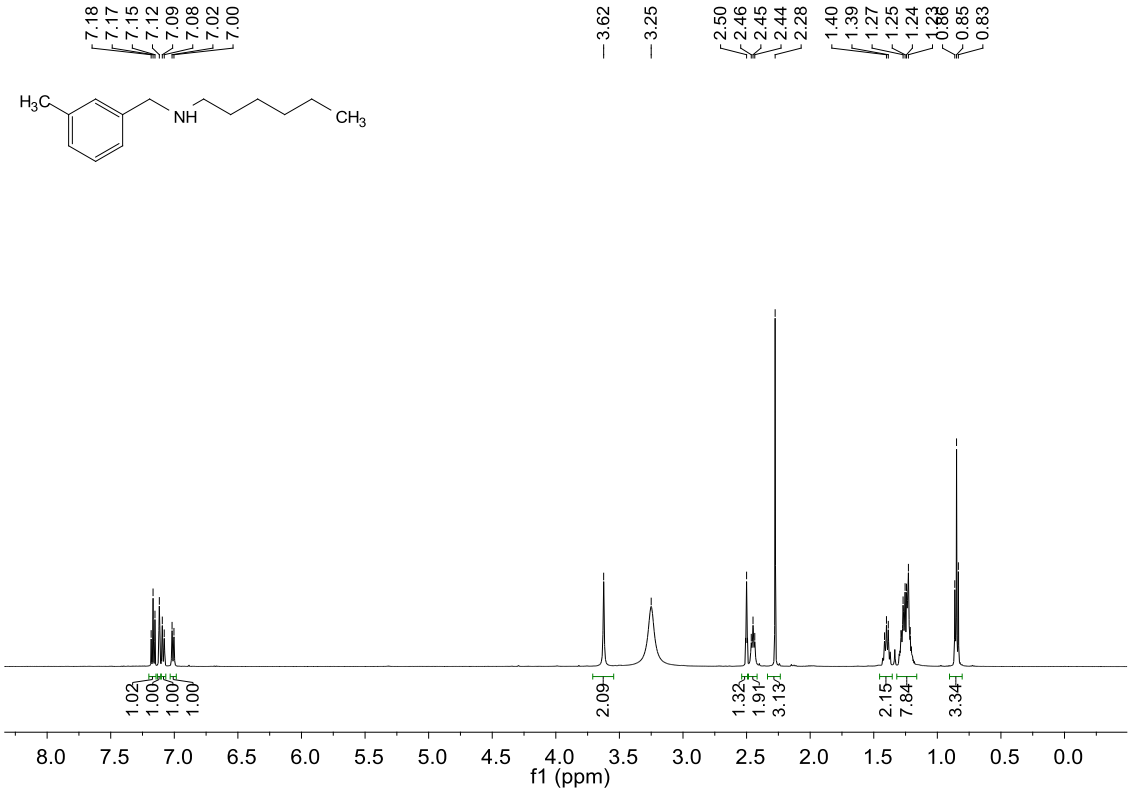


Figure S15. ^{1}H NMR (500 MHz) spectrum of **2g** in DMSO-*d*6

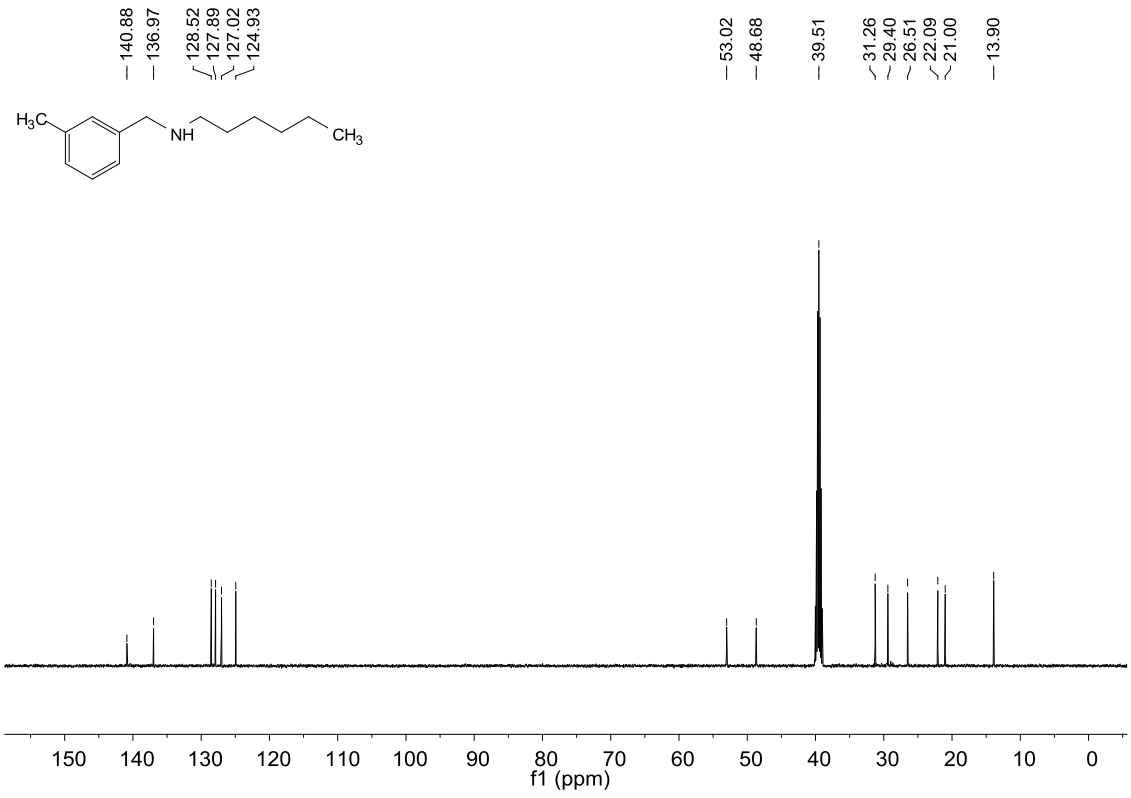


Figure S16. ^{13}C NMR (125 MHz) spectrum of **2g** in DMSO-*d*6

N-(4-methylbenzyl)hexan-1-amine (2h)

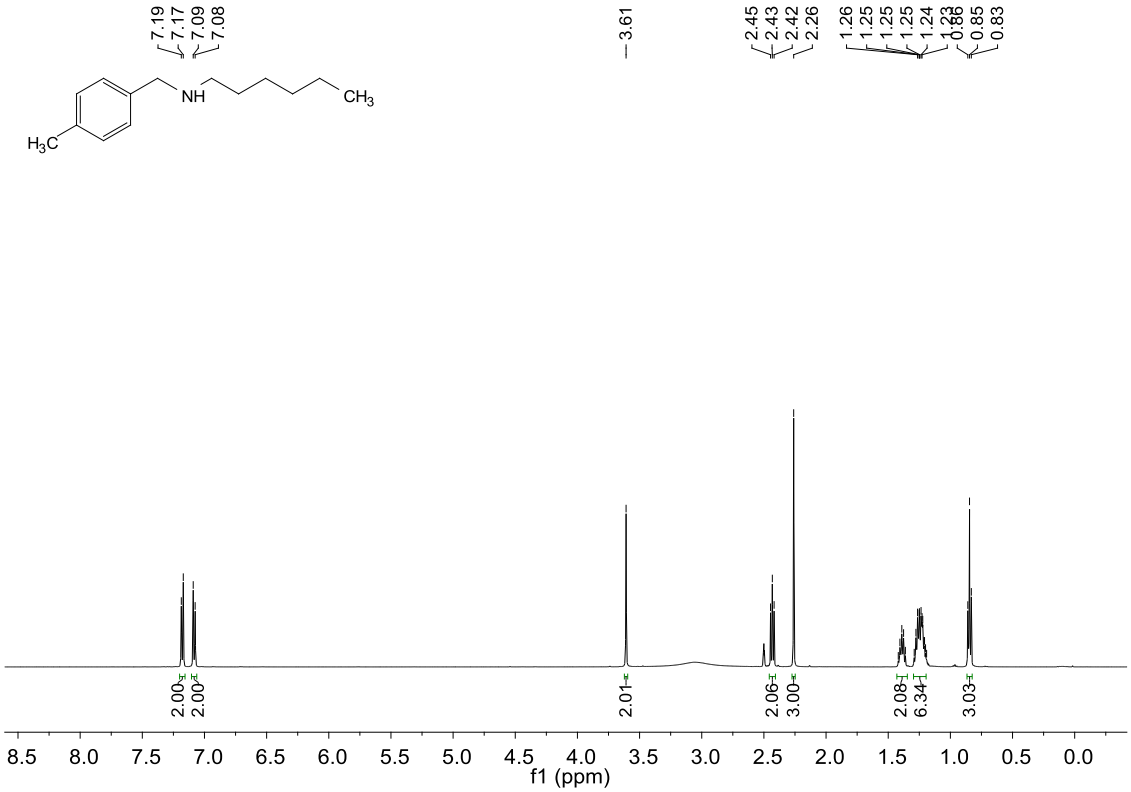


Figure S17. ^{1}H NMR (500 MHz) spectrum of **2h** in DMSO-*d*6

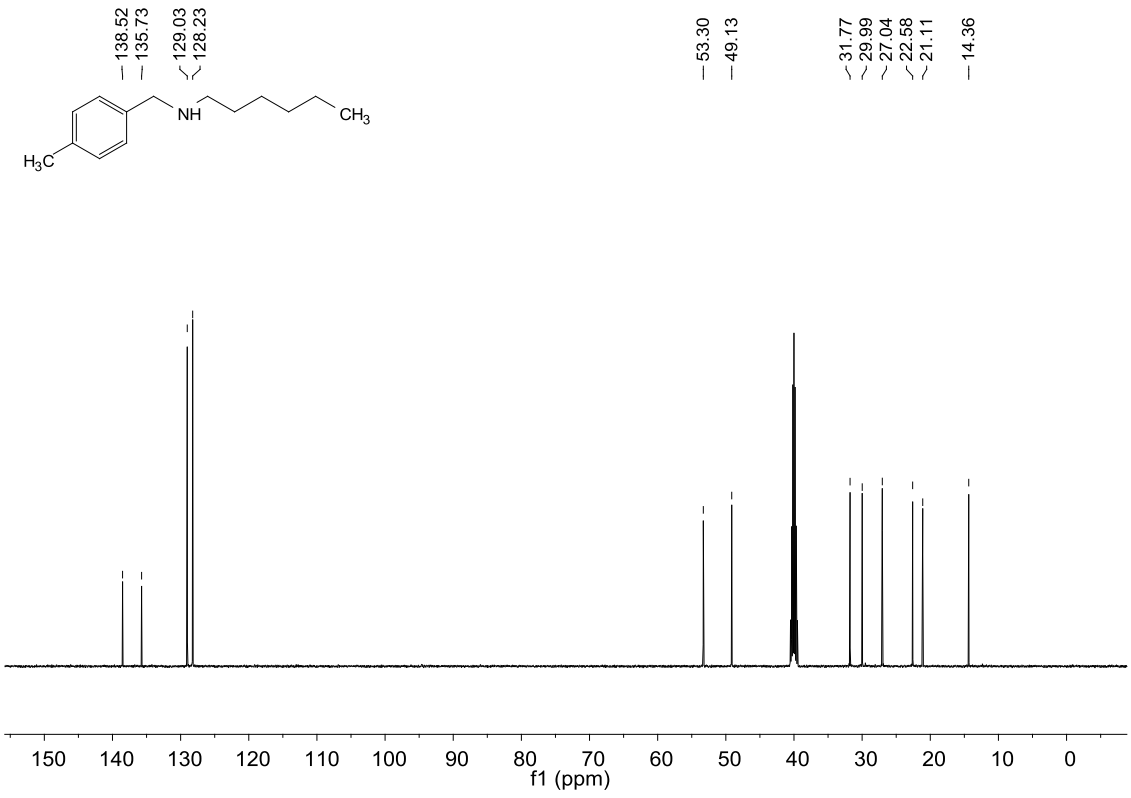


Figure S18. ^{13}C NMR (125 MHz) spectrum of **2h** in DMSO-*d*6

N-(4-fluorobenzyl)hexan-1-amine (2i)

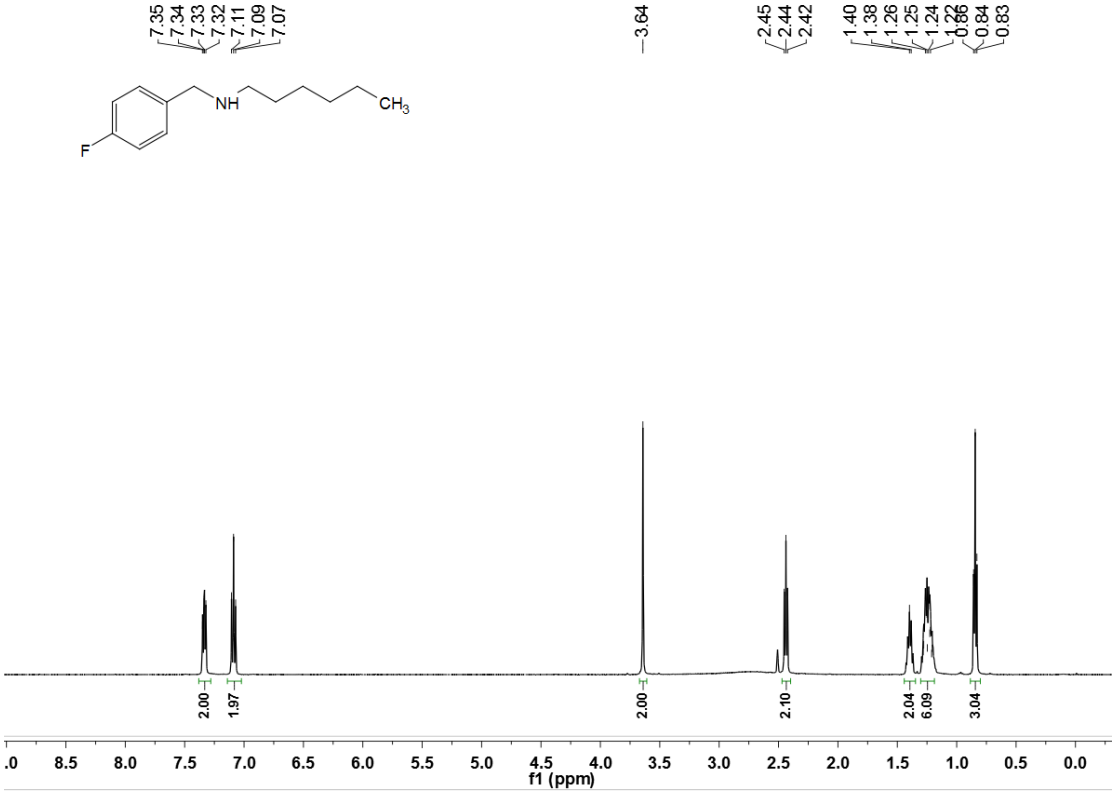


Figure S19. ^{1}H NMR (500 MHz) spectrum of **2i** in DMSO-*d*6

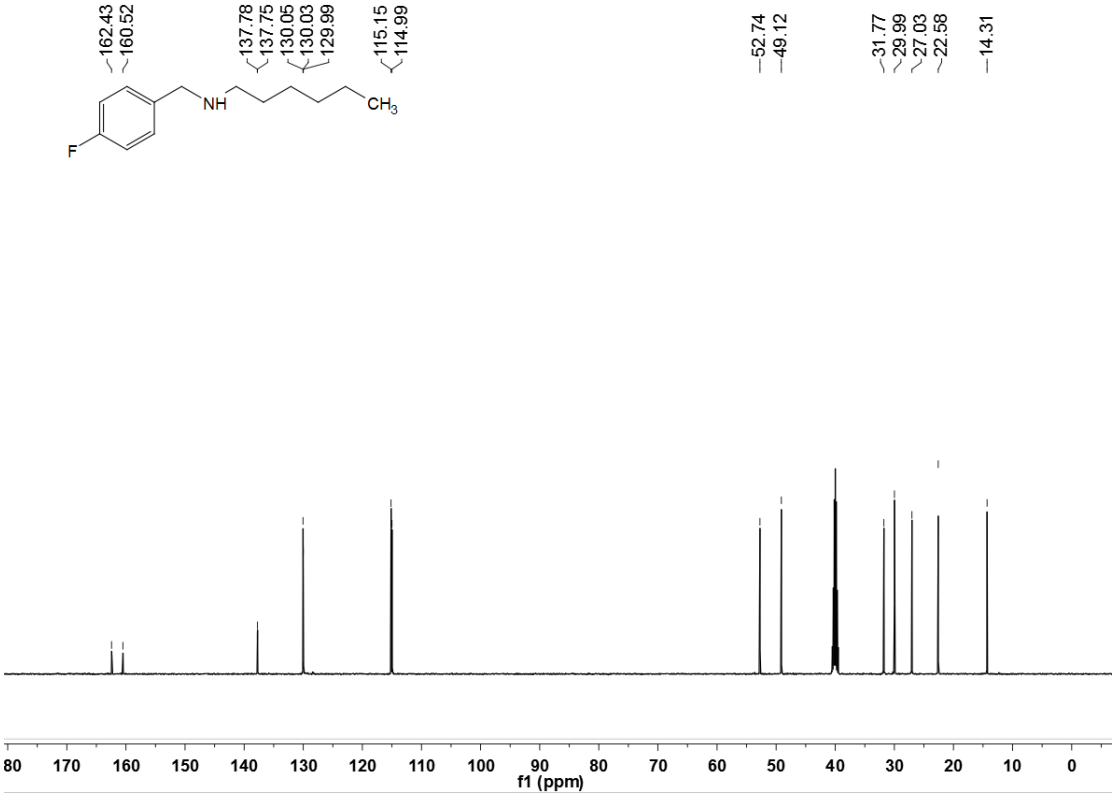


Figure S20. ^{13}C NMR (125 MHz) spectrum of **2i** in DMSO-*d*6

N-(4-(trifluoromethyl)benzyl)propan-1-amine (2j)

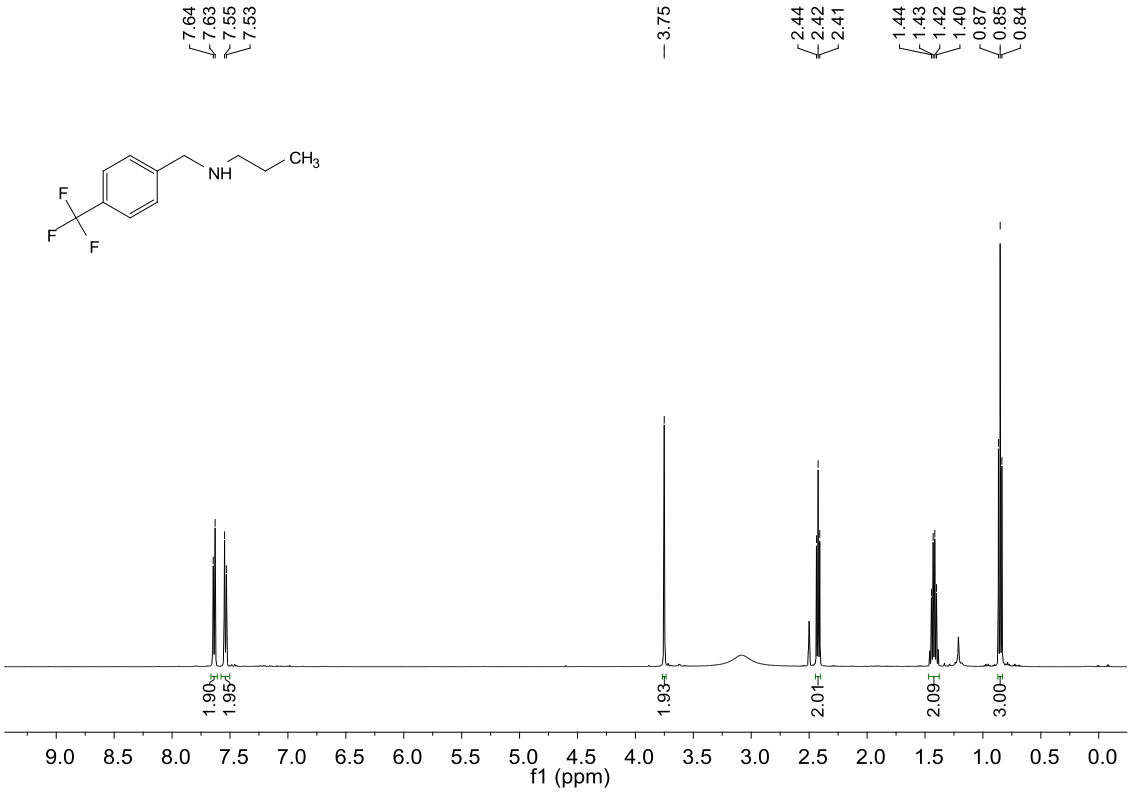


Figure S21. ^{1}H NMR (500 MHz) spectrum of **2j** in DMSO-*d*6

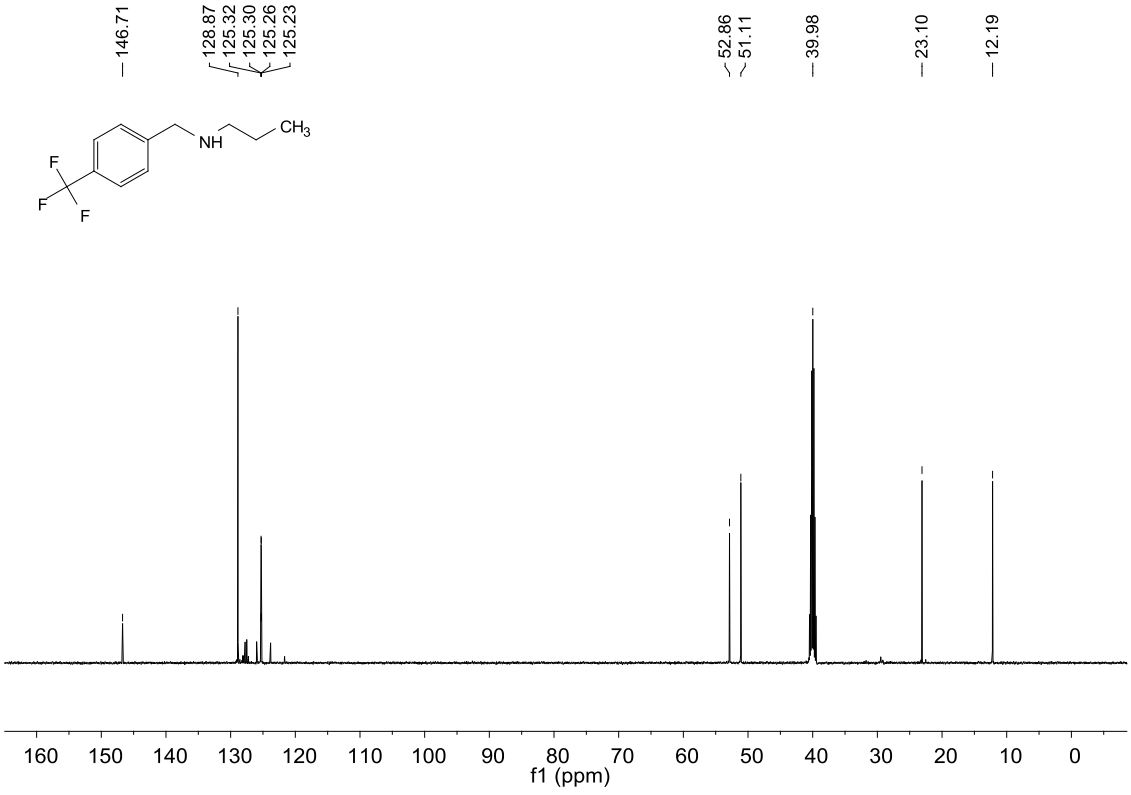


Figure S22. ^{13}C NMR (125 MHz) spectrum of **2j** in DMSO-*d*6

N-(furan-2-ylmethyl)hexan-1-amine (2k)

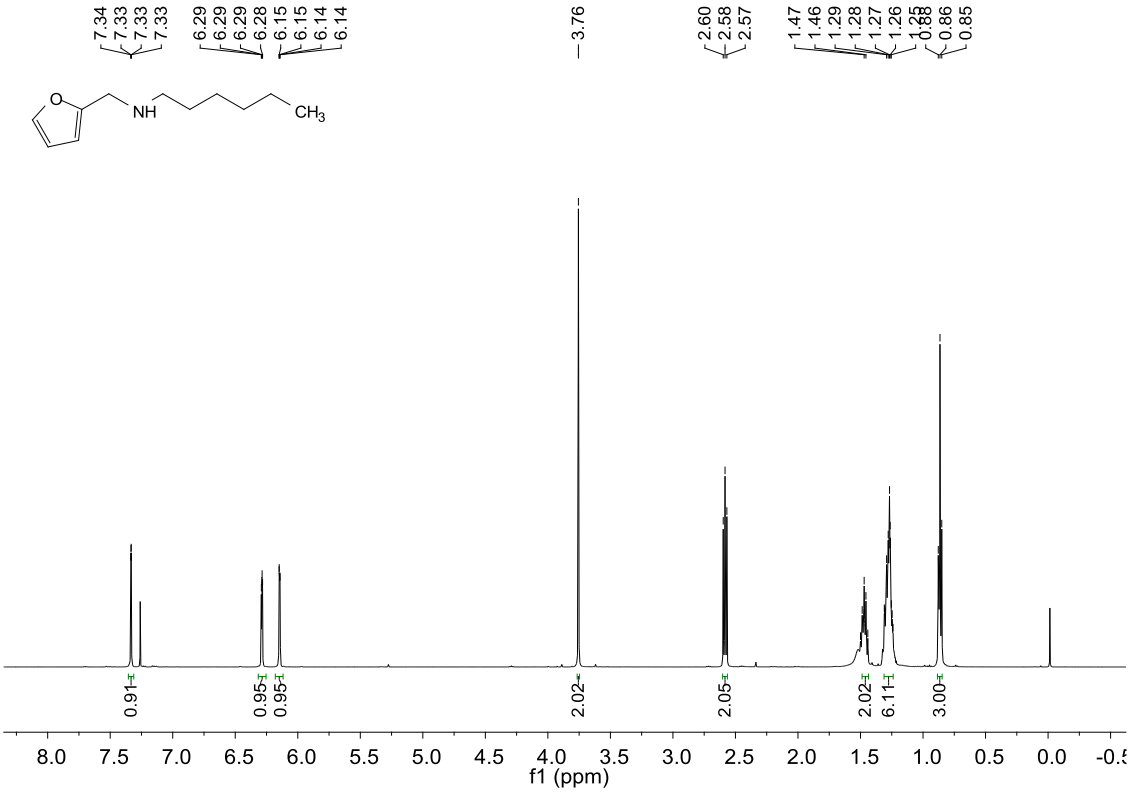


Figure S23. ^{1}H NMR (500 MHz) spectrum of **2k** in $CDCl_3$

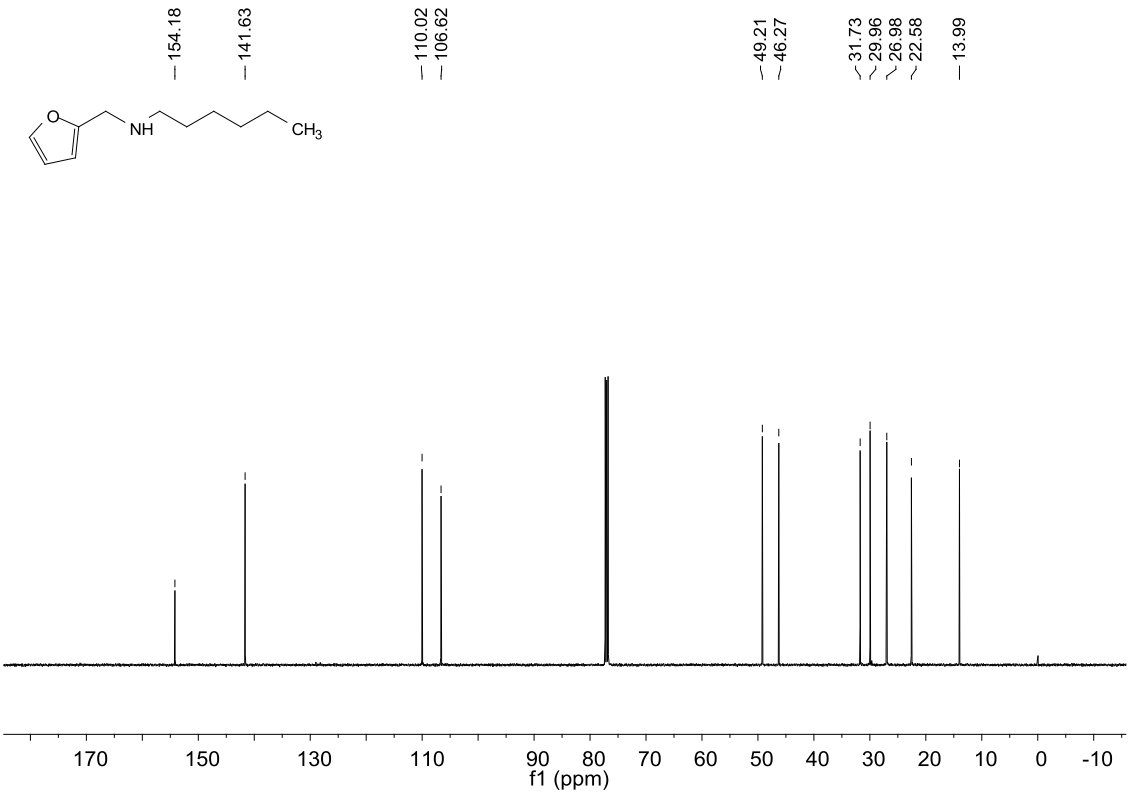


Figure S24 ^{13}C NMR (125 MHz) spectrum of **2k** in $CDCl_3$

N-(thiophen-2-ylmethyl)hexan-1-amine (2l)

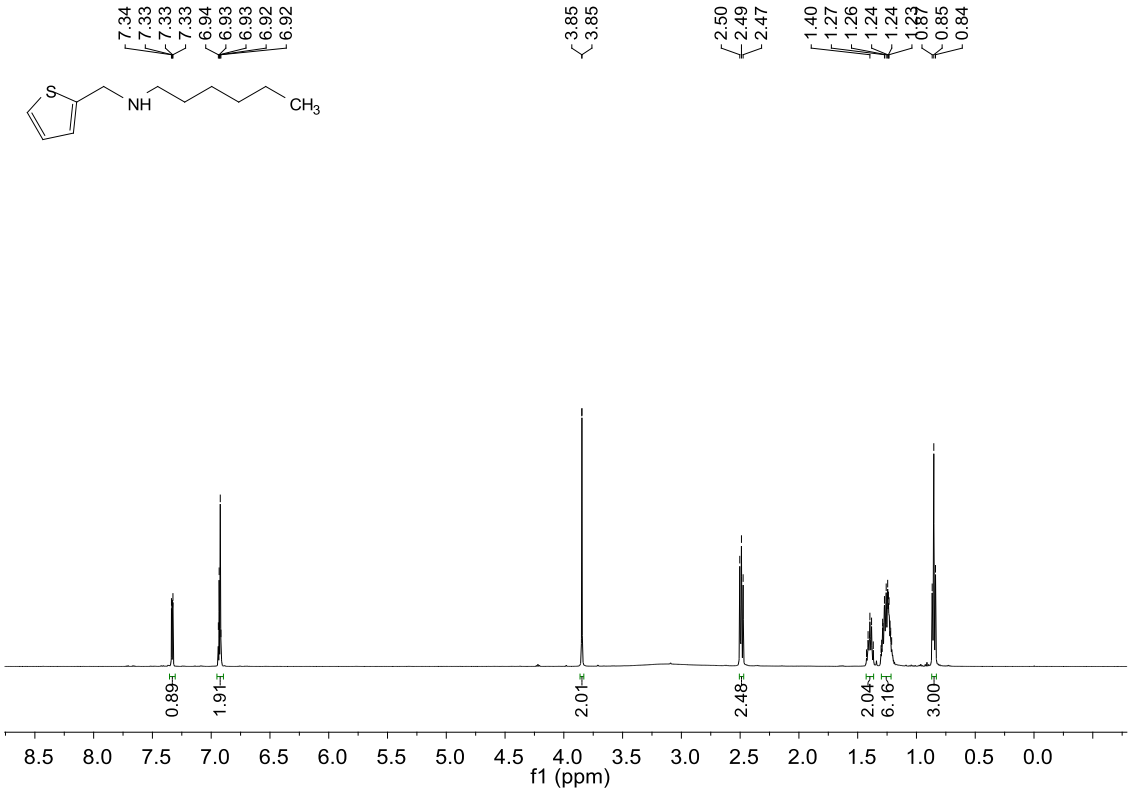


Figure S25. ^{1}H NMR (500 MHz) spectrum of **2l** in DMSO-*d*6

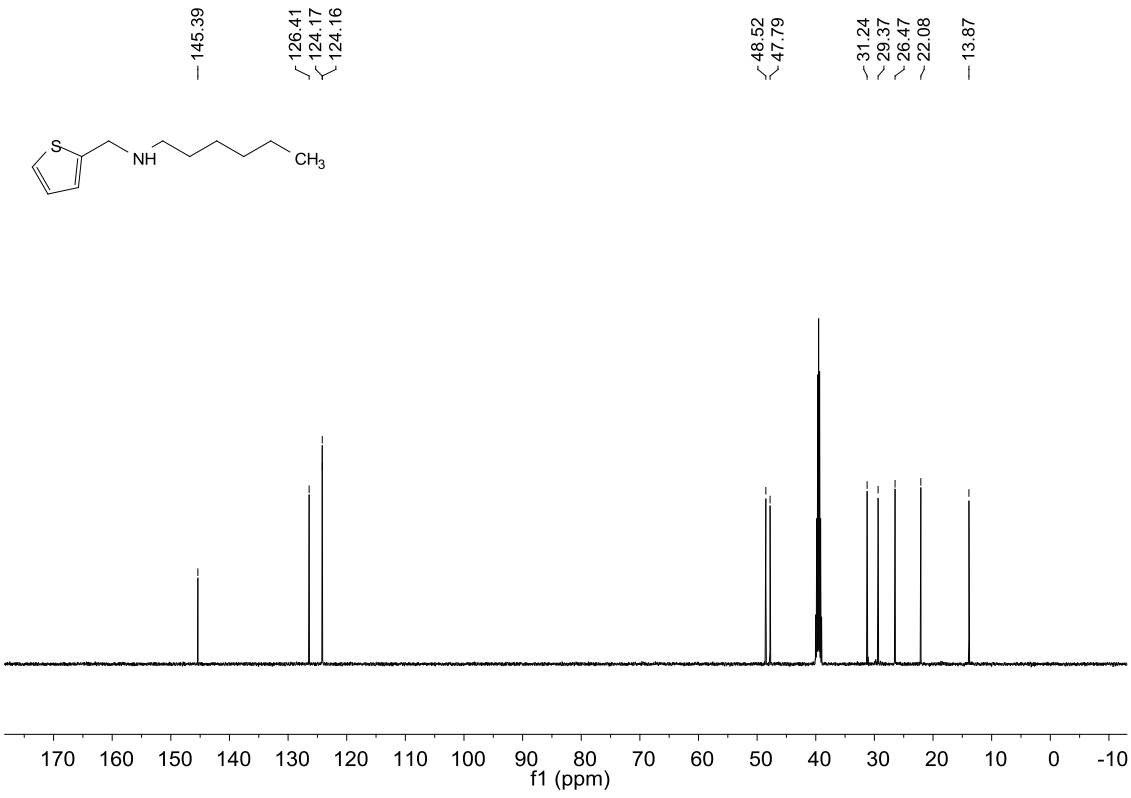


Figure S26 ^{13}C NMR (125 MHz) spectrum of **2l** in DMSO-*d*6

N-benzylaniline (2m)

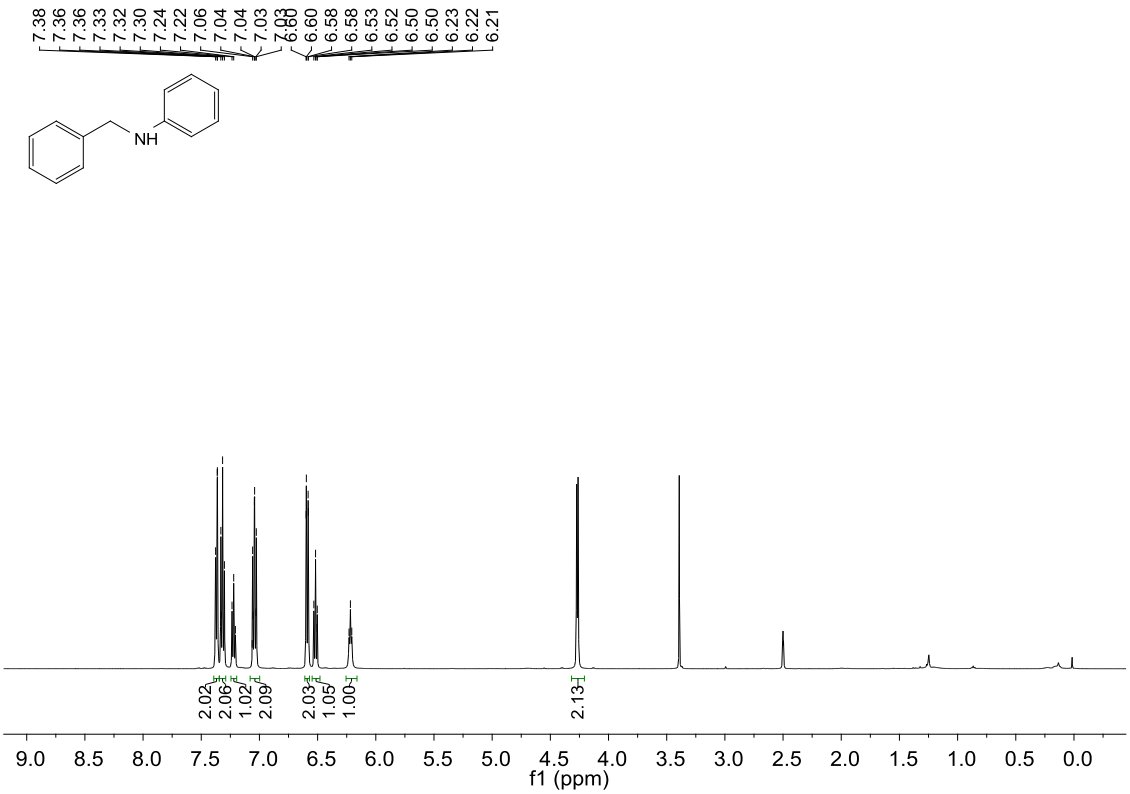


Figure S27. ^{1}H NMR (500 MHz) spectrum of **2m** in DMSO-*d*6

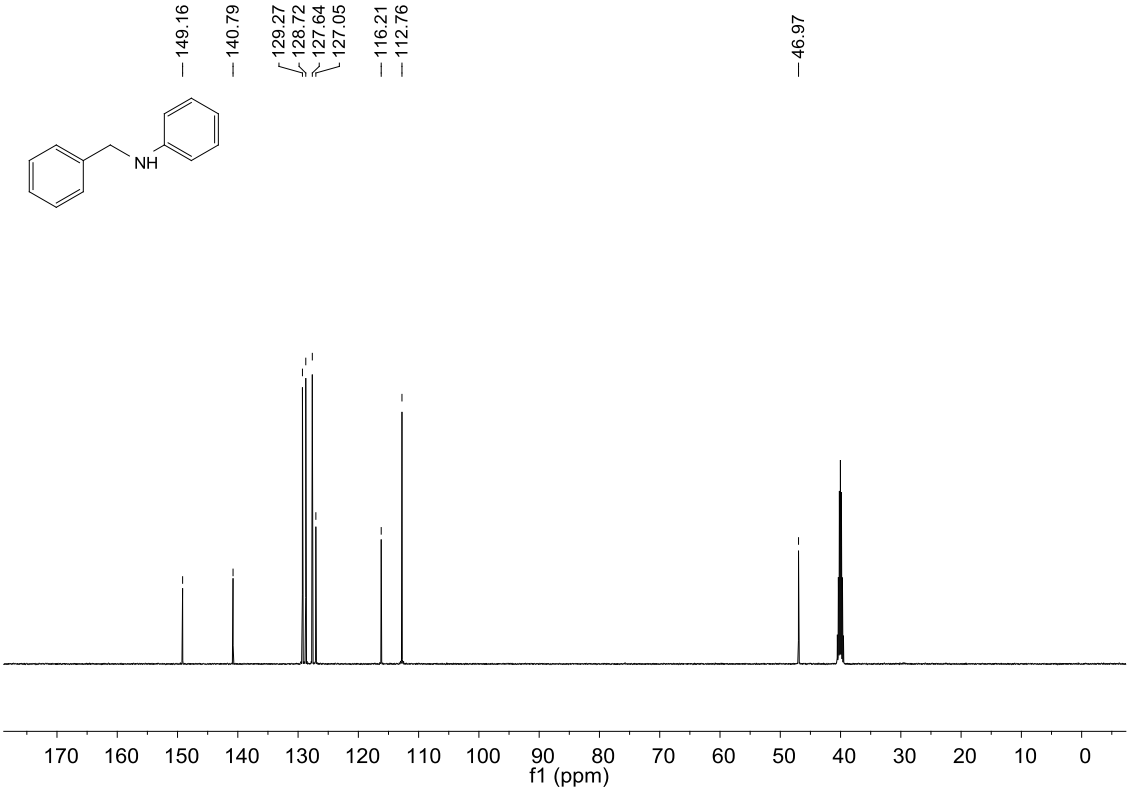


Figure S28 ^{13}C NMR (125 MHz) spectrum of **2m** in DMSO-*d*6

N-benzyl-2,6-dimethylaniline (2n)

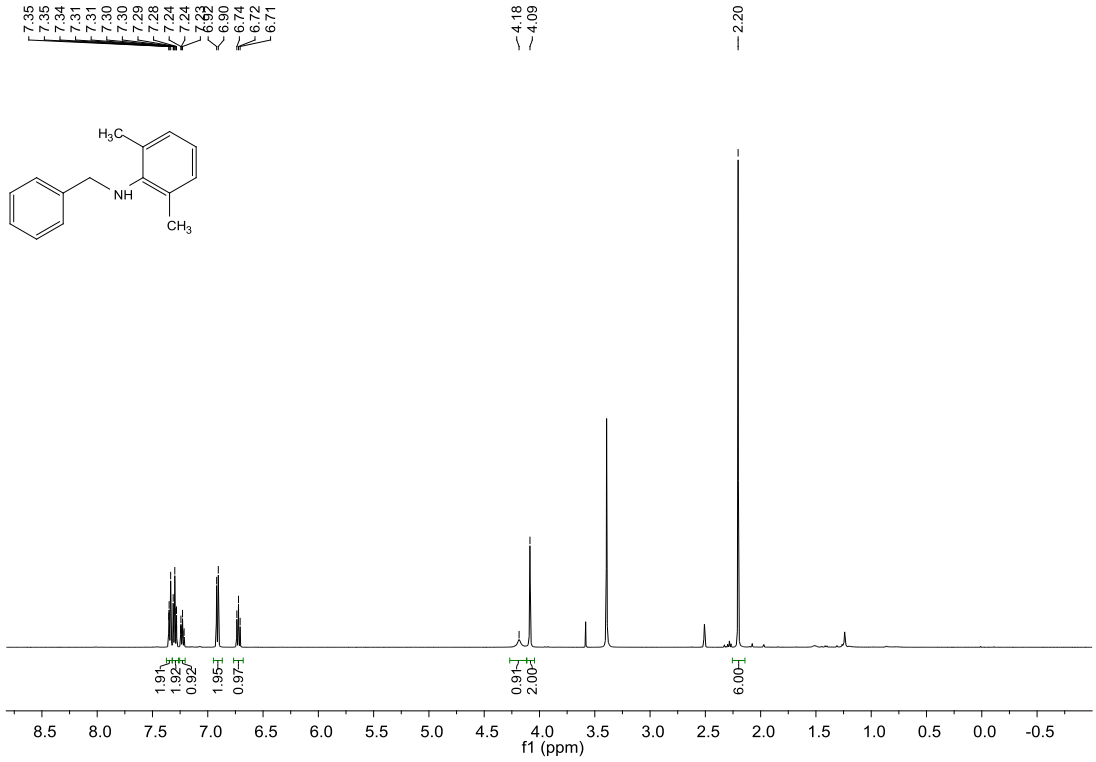


Figure S29. ^{1}H NMR (500 MHz) spectrum of **2n** in DMSO-*d*6

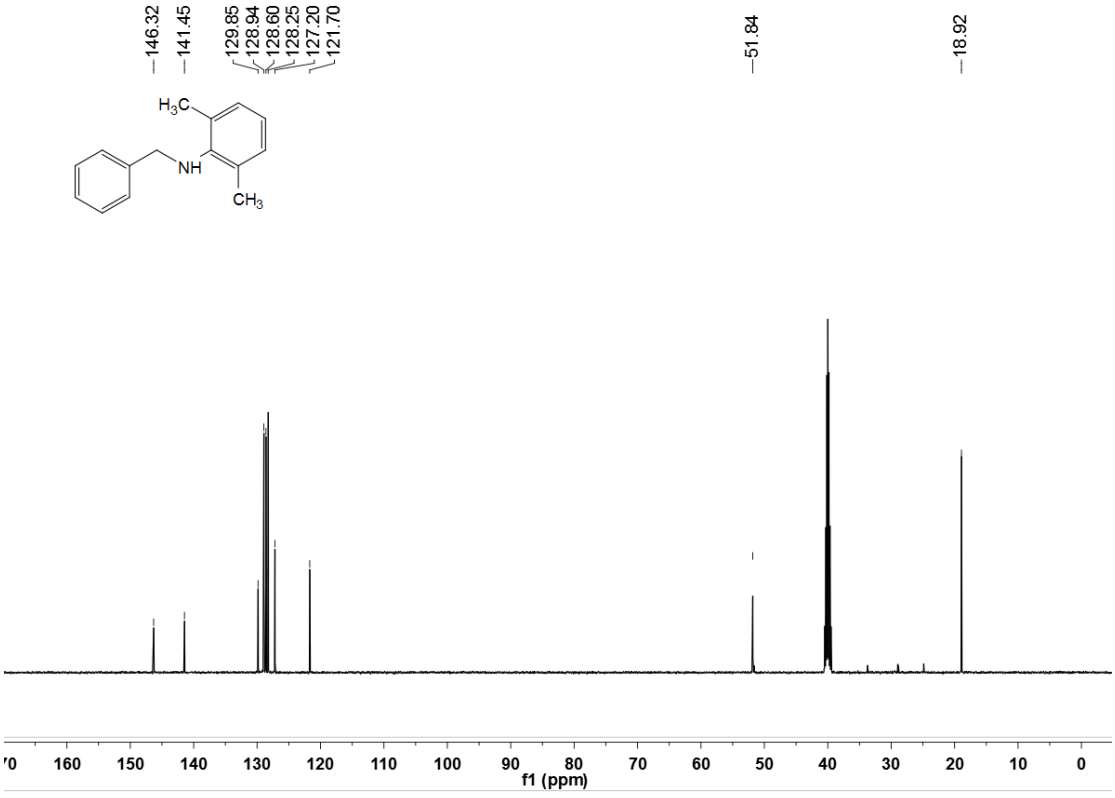


Figure S30 ^{13}C NMR (125 MHz) spectrum of **2n** in DMSO-*d*6

N-ethylaniline (4a)

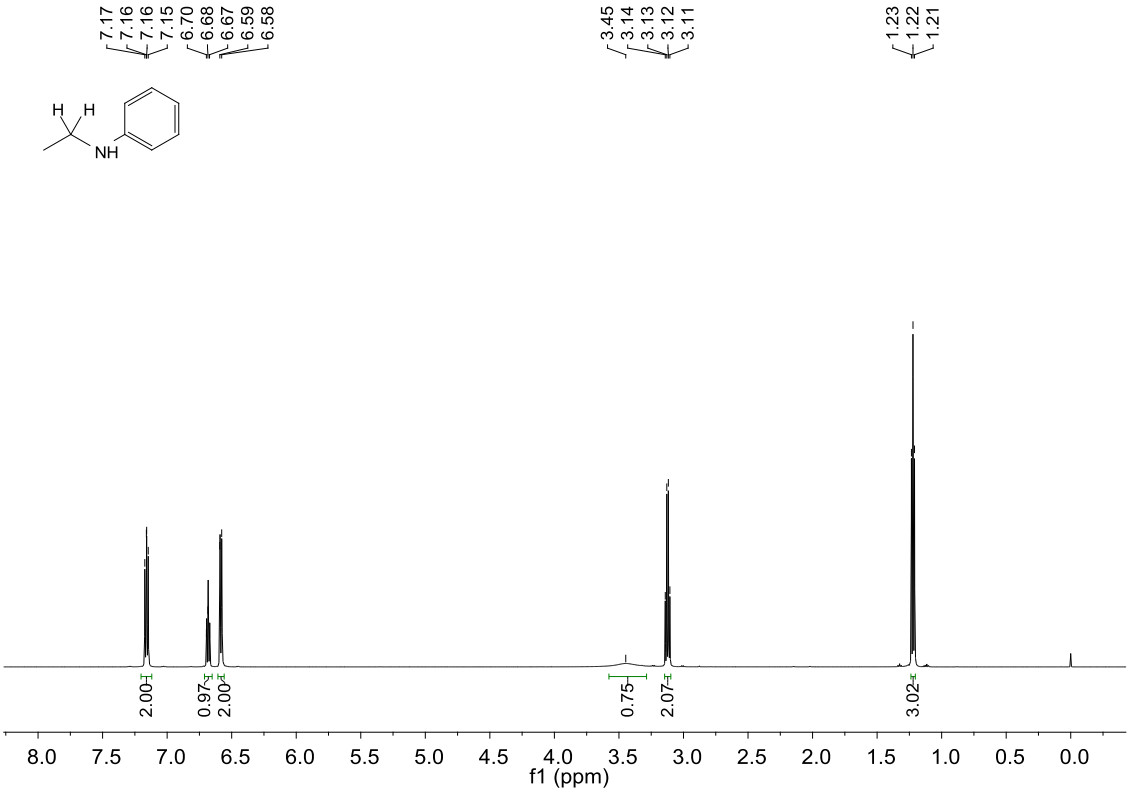


Figure S31. ^{1}H NMR (600 MHz) spectrum of **4a** in $CDCl_3$

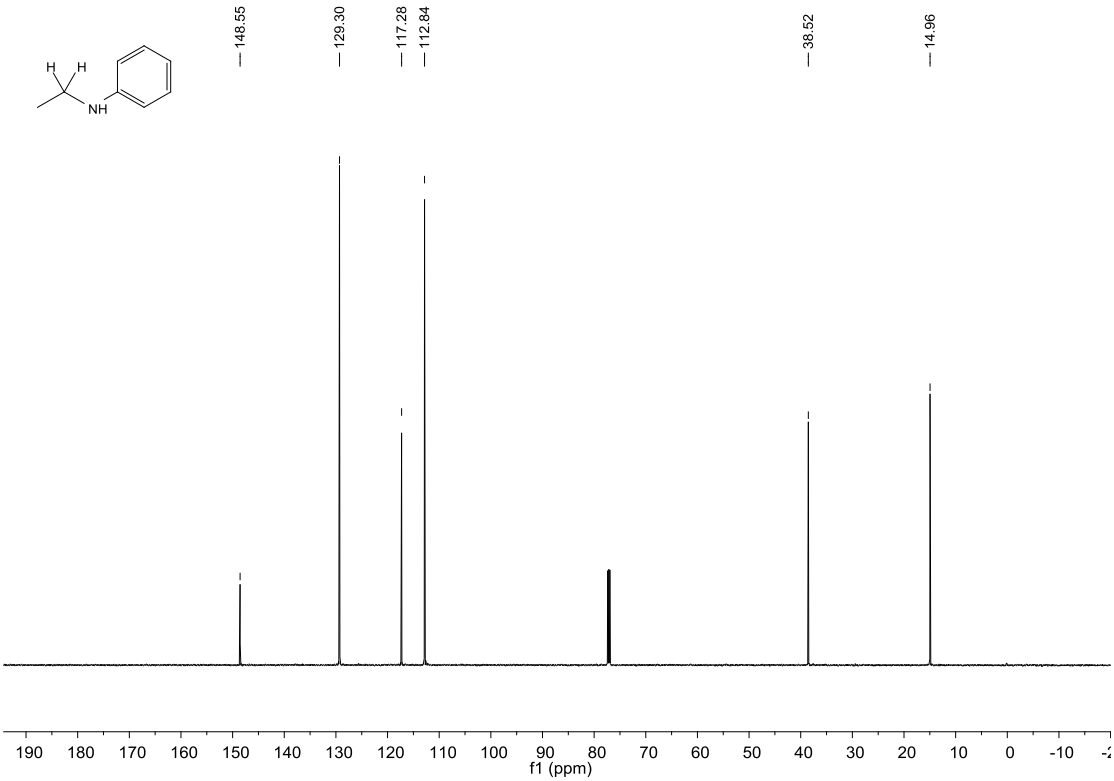


Figure S32 ^{13}C NMR (150 MHz) spectrum of **4a** in $CDCl_3$

N-ethyl-4-methoxyaniline (4b)

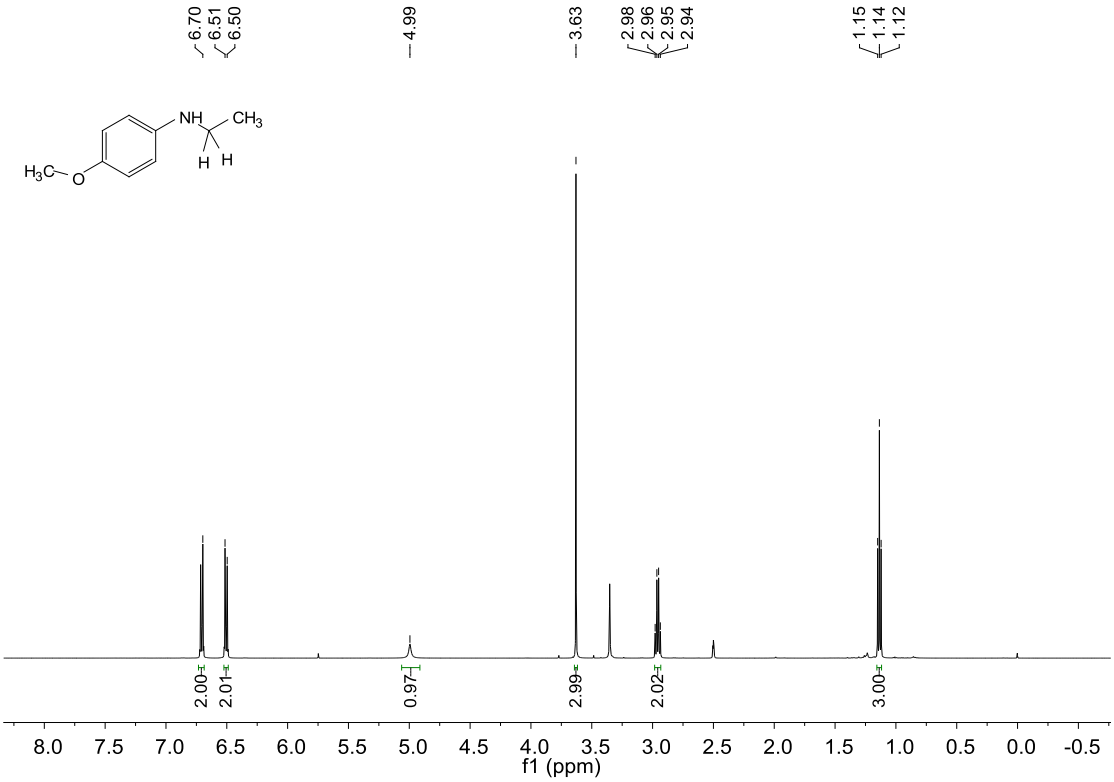


Figure S33. ^{1}H NMR (500 MHz) spectrum of **4b** in DMSO-*d*6

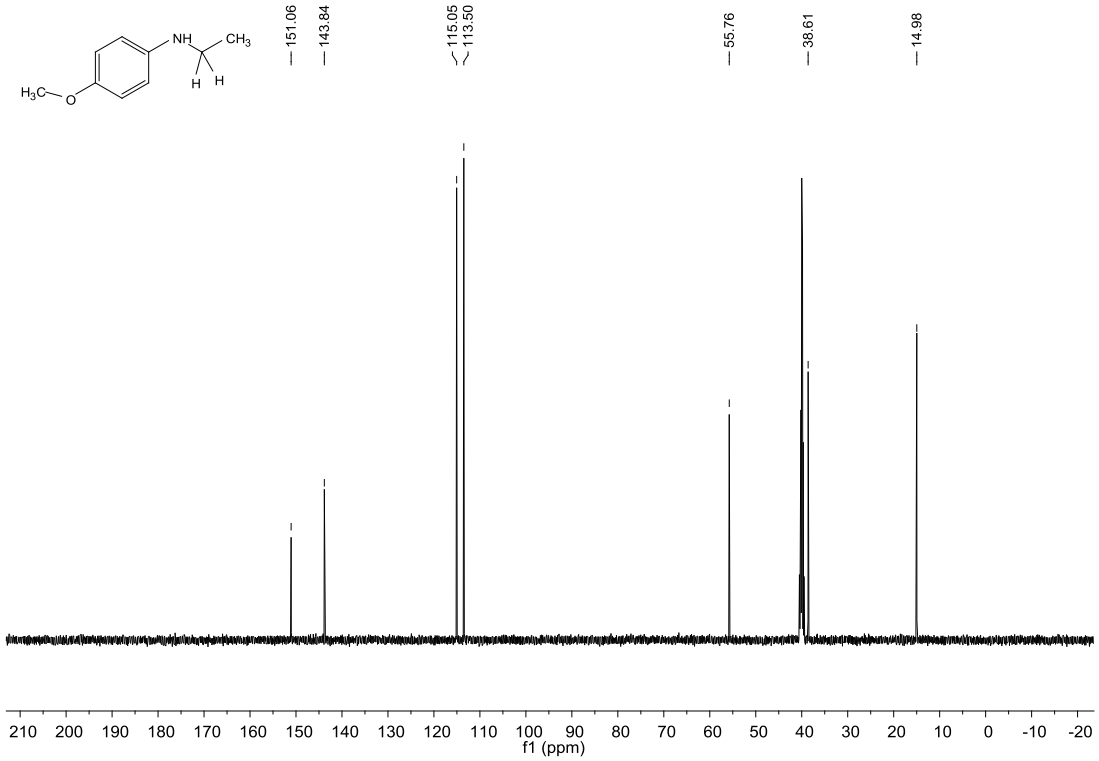


Figure S34 ^{13}C NMR (125 MHz) spectrum of **4b** in DMSO-*d*6

N-ethyl-4-fluoroaniline (4c)

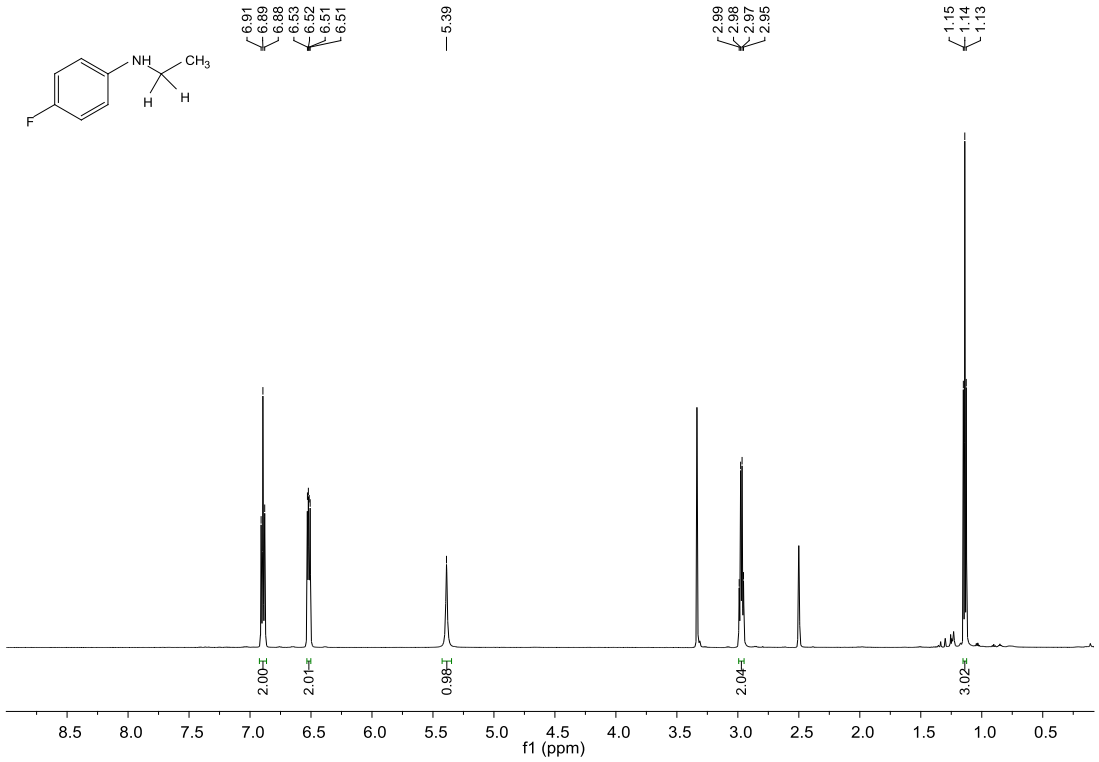


Figure S35. ^{1}H NMR (600 MHz) spectrum of **4c** in DMSO-*d*6

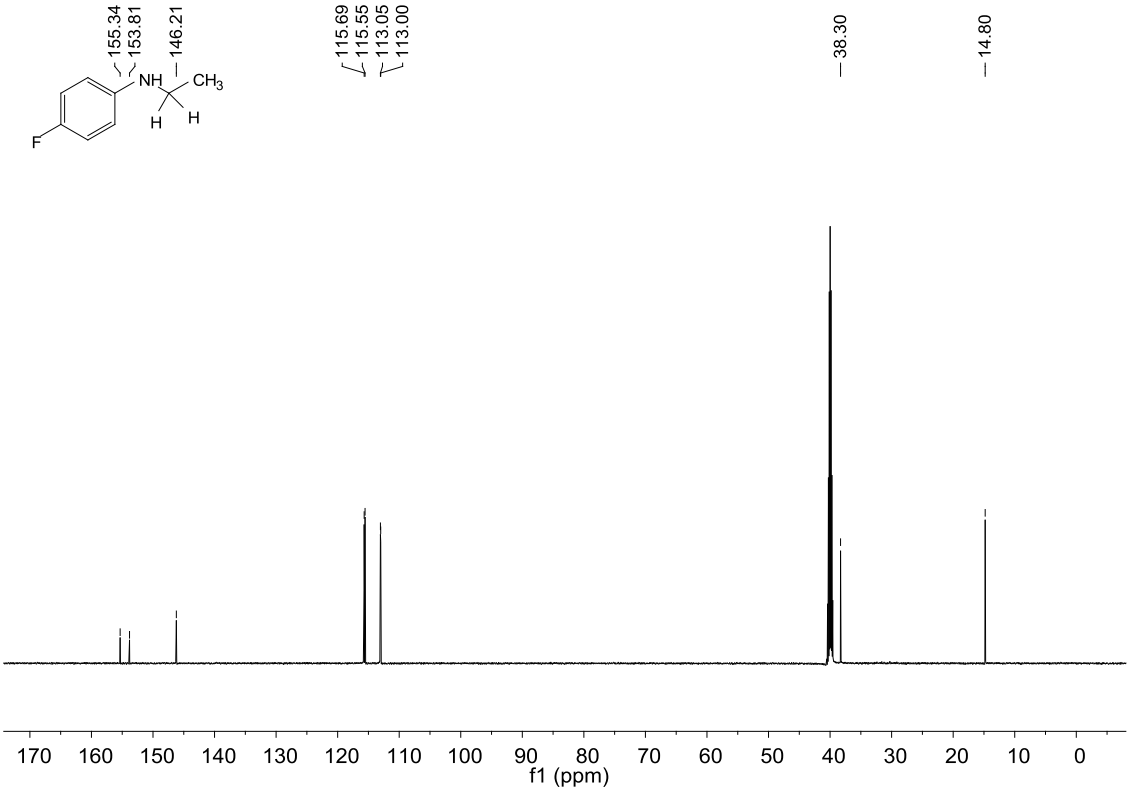


Figure S36 ^{13}C NMR (150 MHz) spectrum of **4c** in DMSO-*d*6

4-bromo-N-ethylaniline (4d)

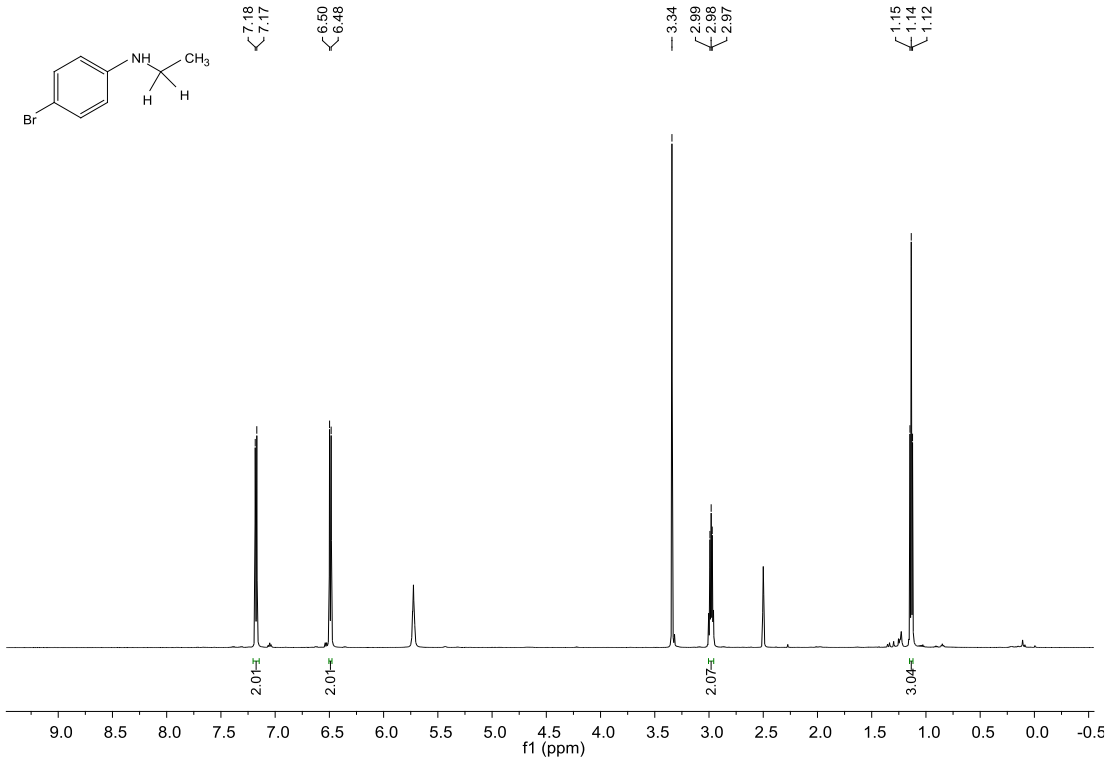


Figure S37. ^{1}H NMR (600 MHz) spectrum of **4d** in DMSO-*d*6

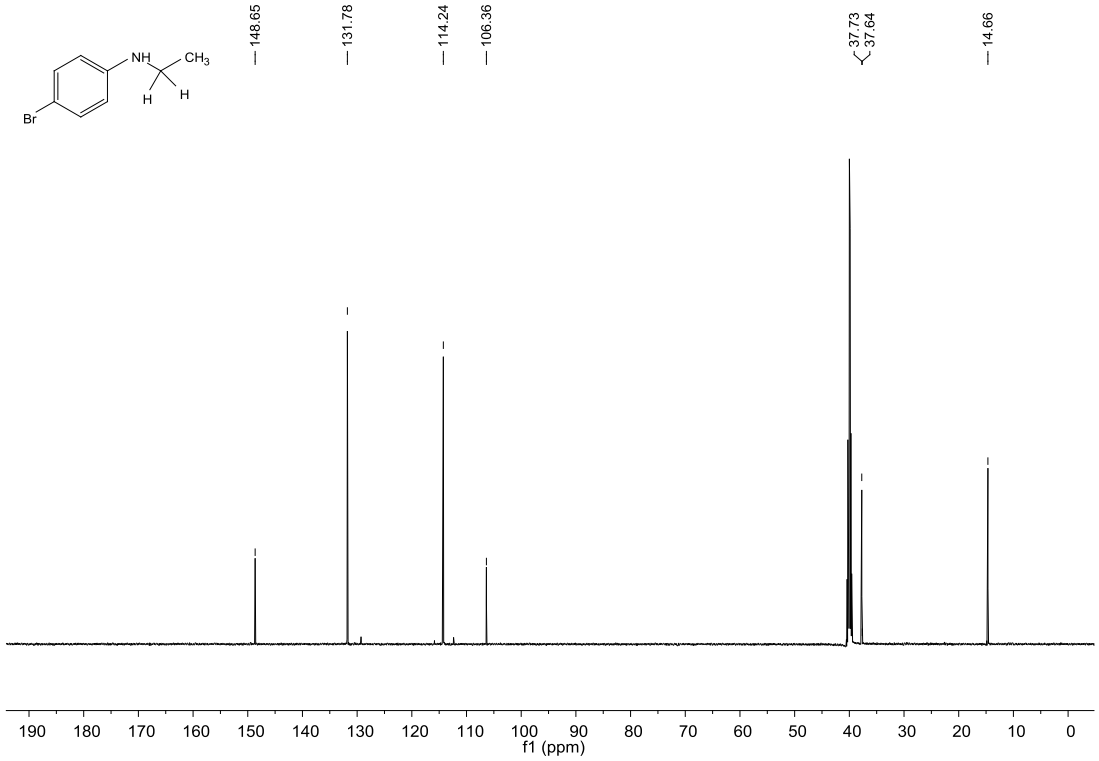


Figure S38 ^{13}C NMR (150 MHz) spectrum of **4d** in DMSO-*d*6

N-ethylnaphthalen-1-amine (4e)

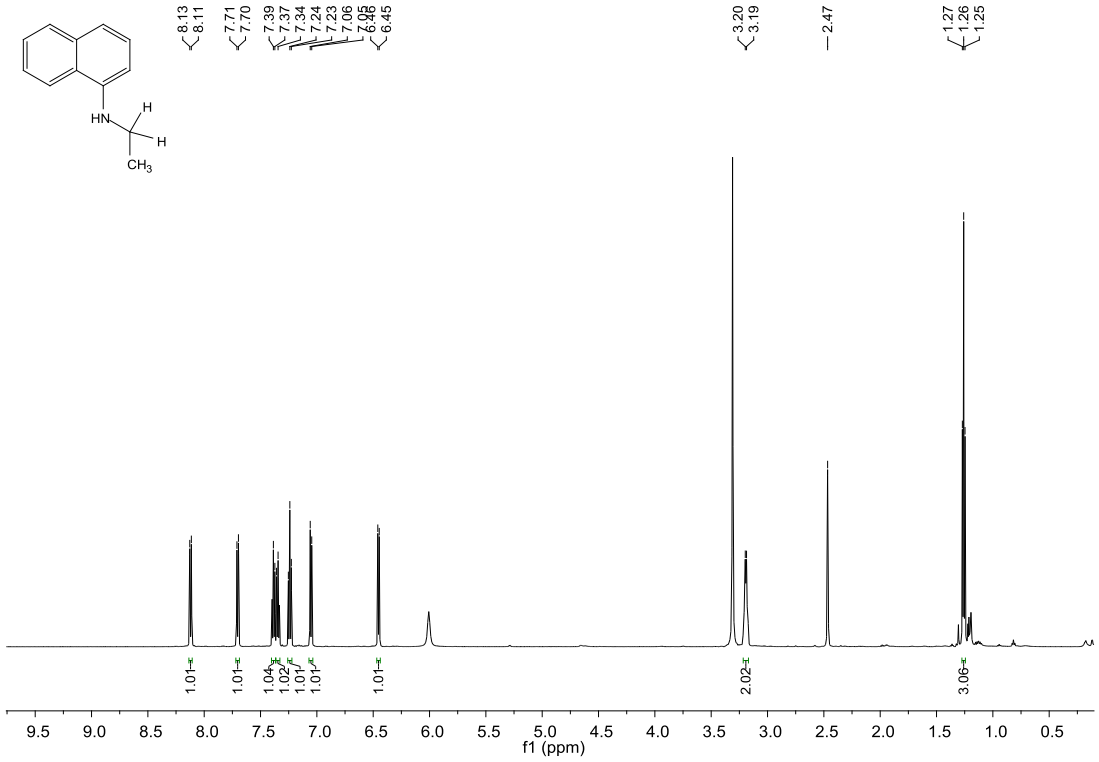


Figure S39. ^{1}H NMR (600 MHz) spectrum of **4d** in DMSO-*d*6

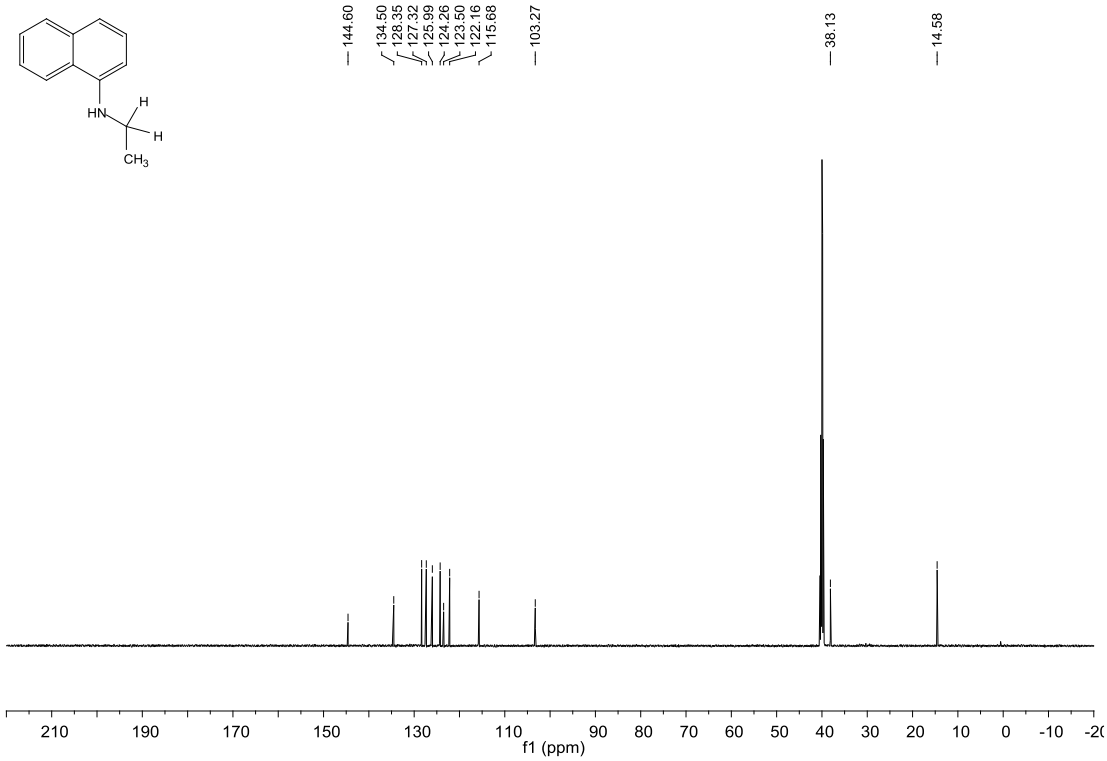


Figure S40 ^{13}C NMR (150 MHz) spectrum of **4d** in DMSO-*d*6

2,6-dimethyl-*N*-propylaniline (4f)

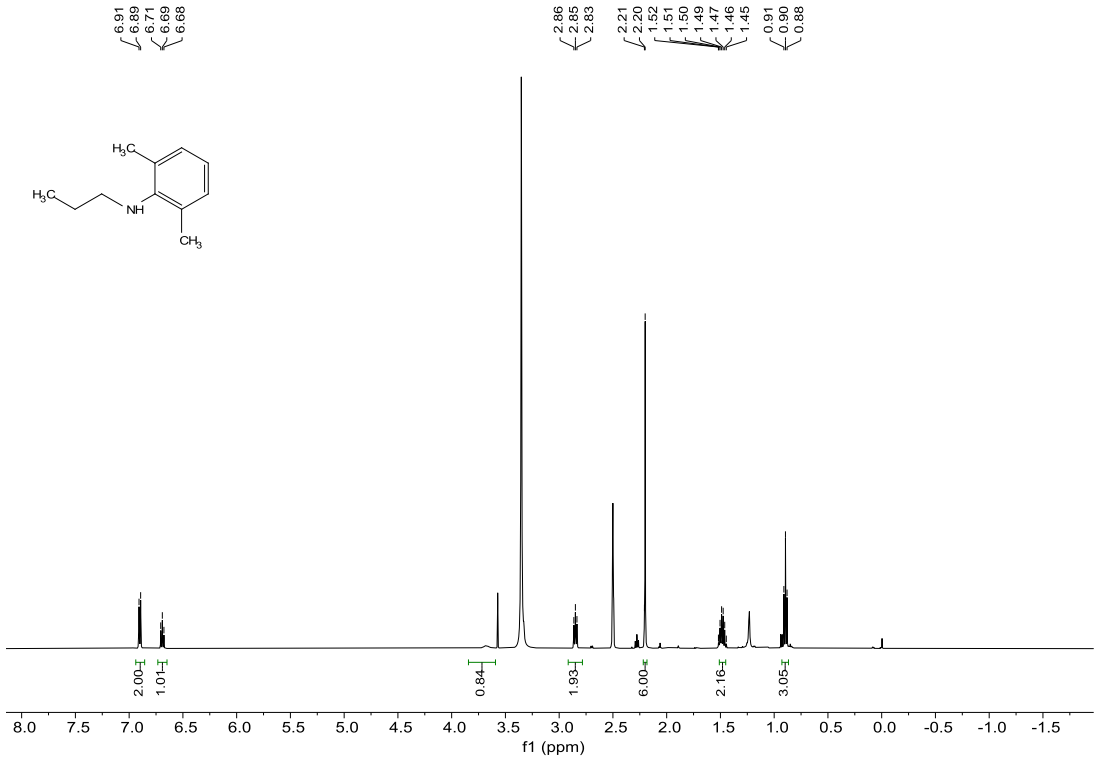


Figure S41. ^{1}H NMR (500 MHz) spectrum of **4f** in DMSO-*d*6

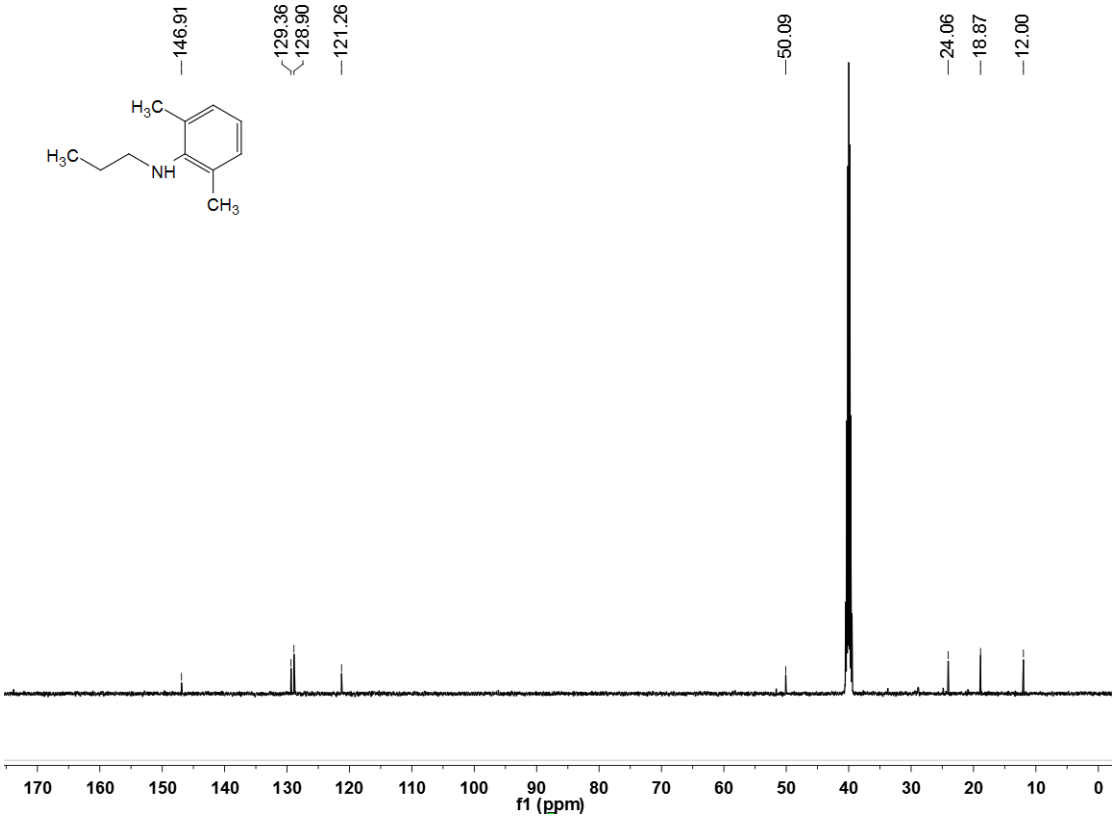


Figure S42 ^{13}C NMR (125 MHz) spectrum of **4f** in DMSO-*d*6

N-isobutyl-2,6-dimethylaniline (4g)

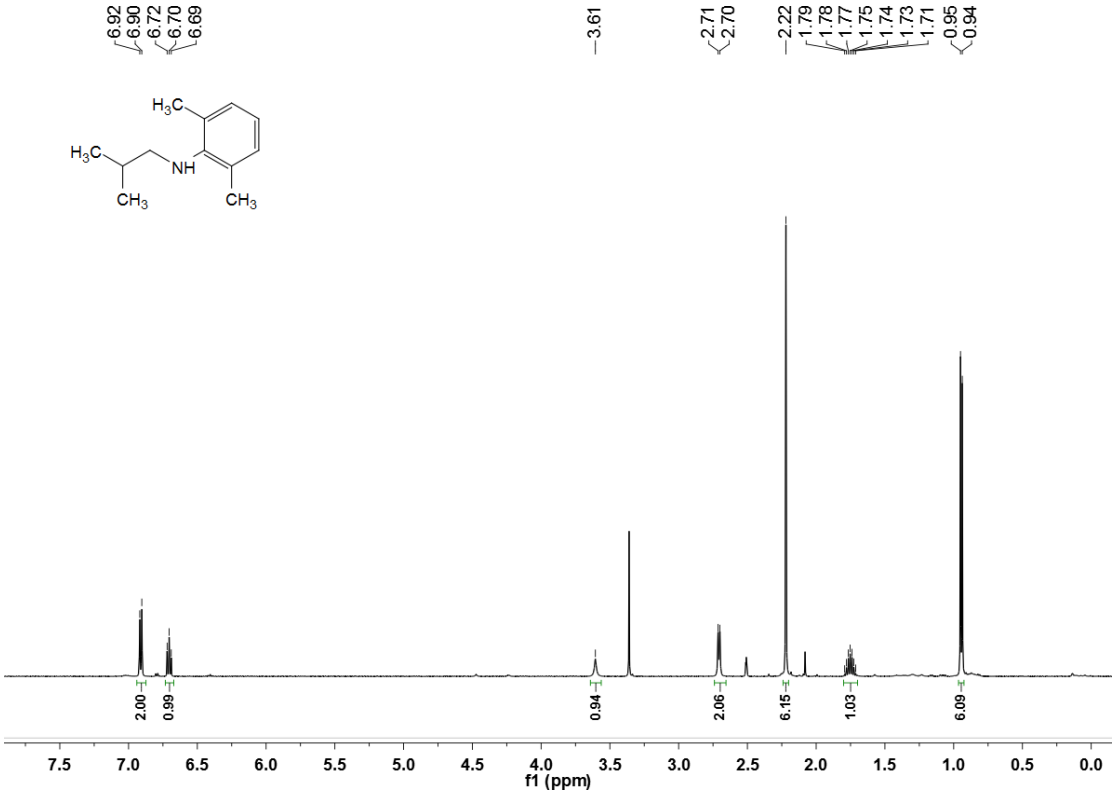


Figure S43. ^{1}H NMR (500 MHz) spectrum of **4g** in DMSO-*d*6

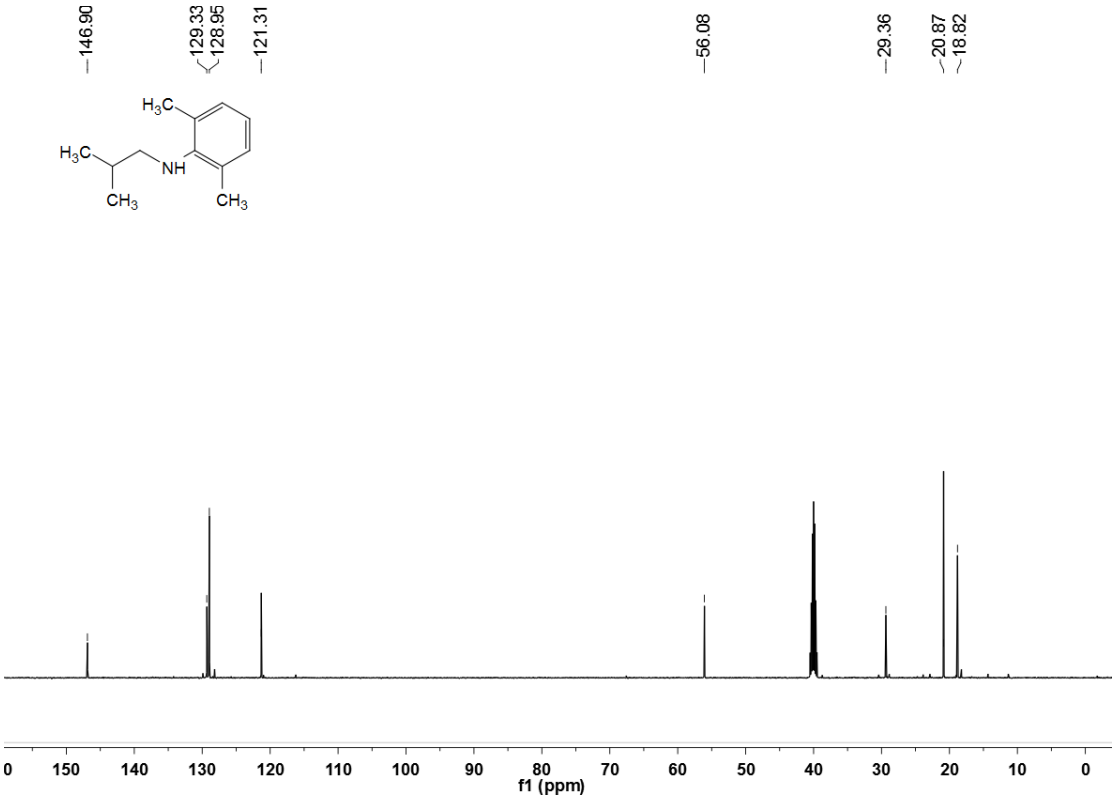


Figure S44 ^{13}C NMR (125 MHz) spectrum of **4g** in DMSO-*d*6

N-benzylethanamine (4h)

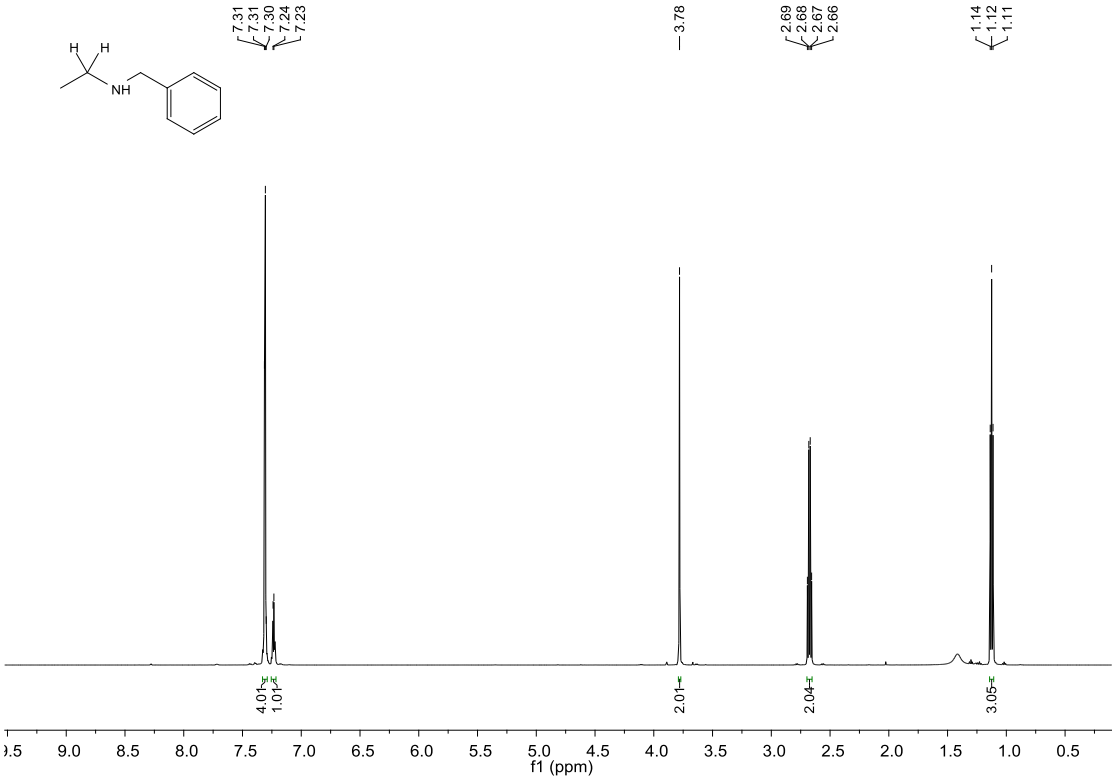


Figure S45. ^{1}H NMR (600 MHz) spectrum of **4h** in $CDCl_3$

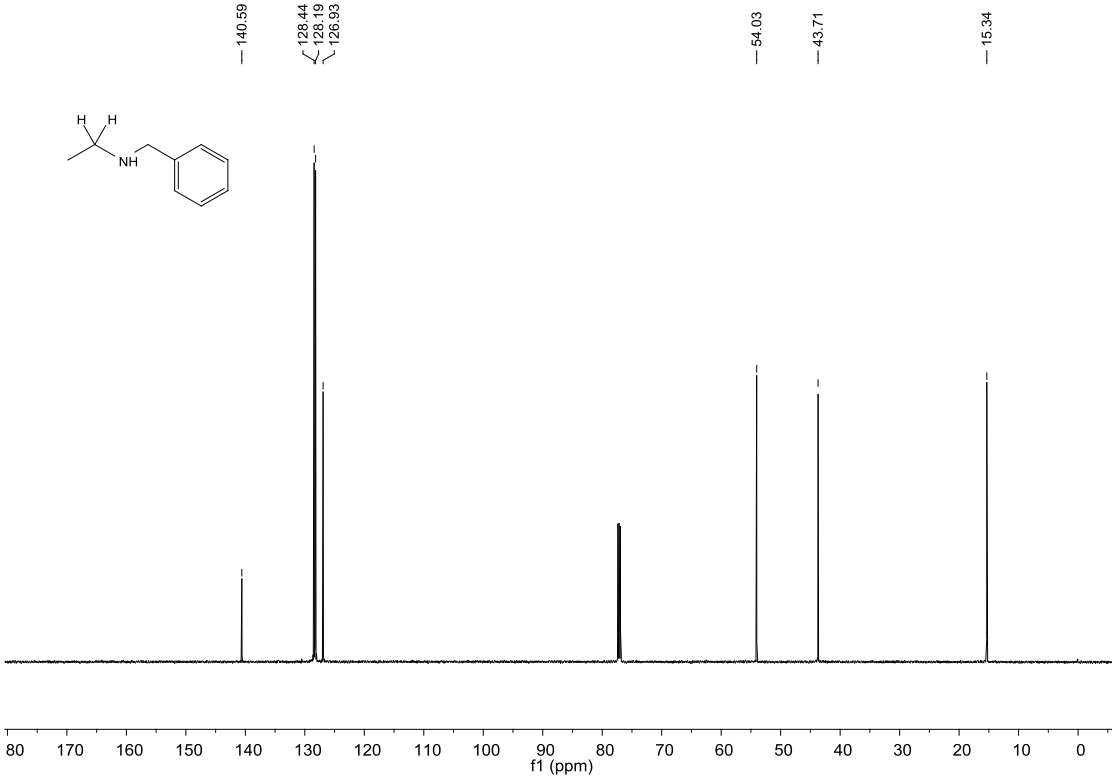


Figure S46 ^{13}C NMR (150 MHz) spectrum of **4h** in $CDCl_3$

N-benzylhexan-1-amine (4i)

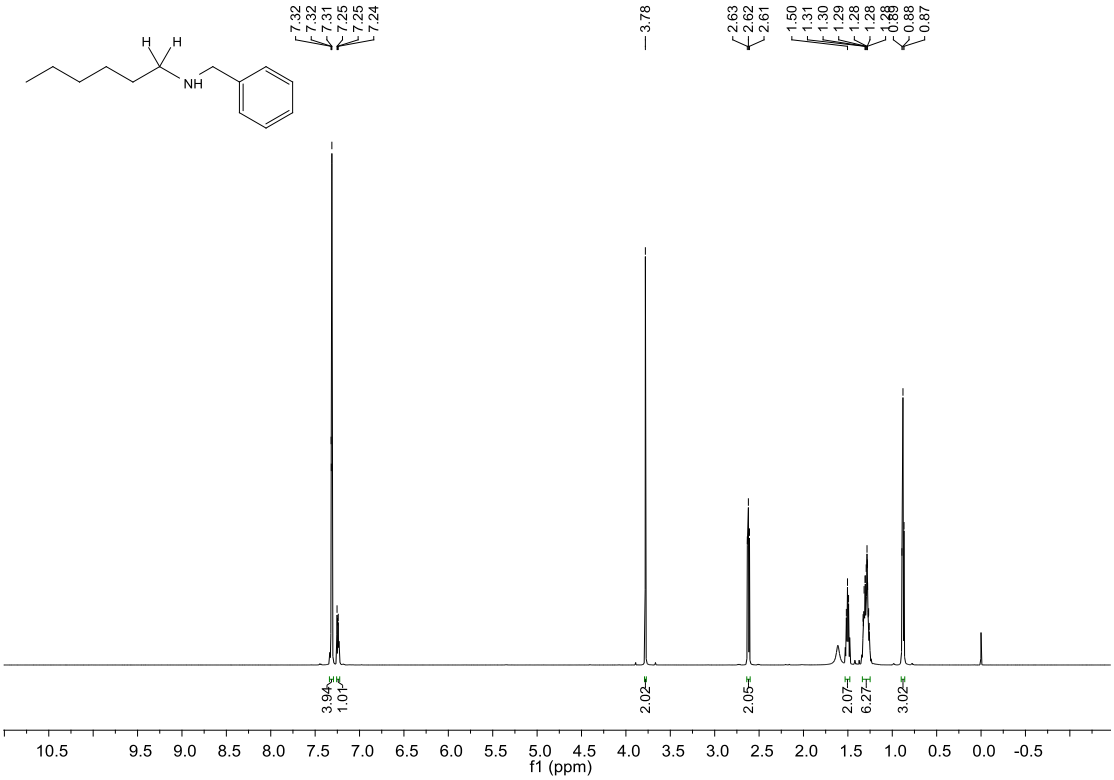


Figure S47. ^{1}H NMR (600 MHz) spectrum of **4i** in $CDCl_3$

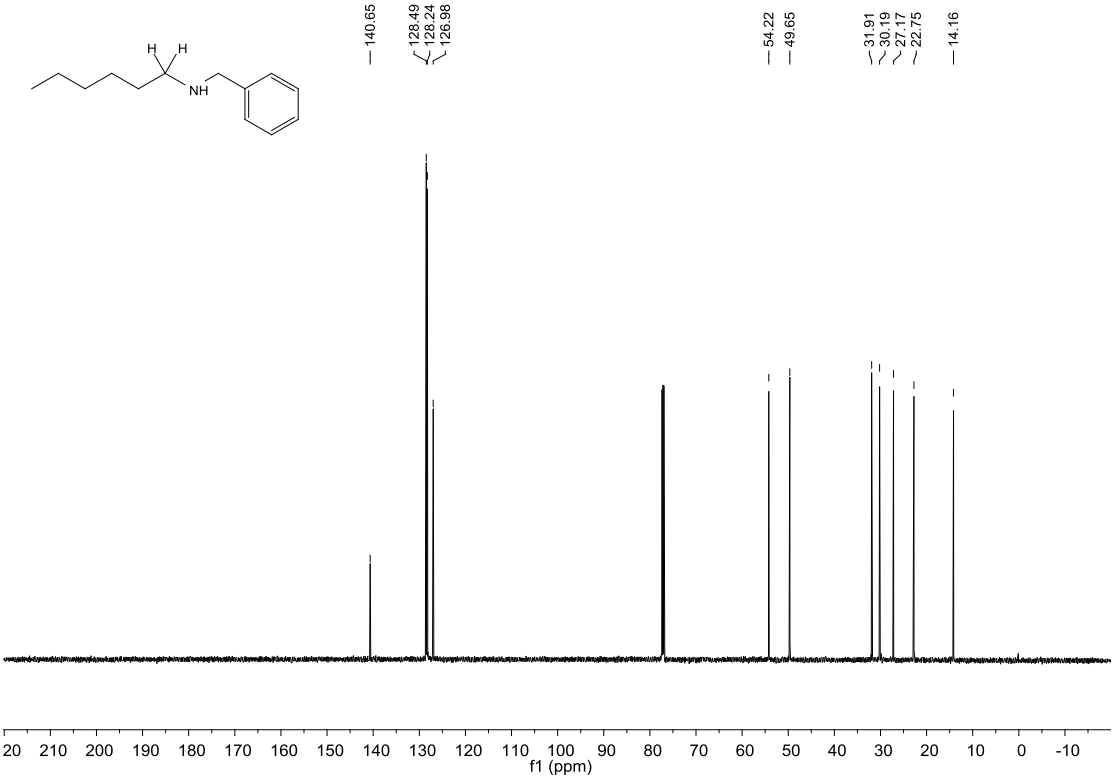


Figure S48 ^{13}C NMR (150 MHz) spectrum of **4i** in $CDCl_3$

N-benzyl-1-cyclohexylmethanamine (4j)

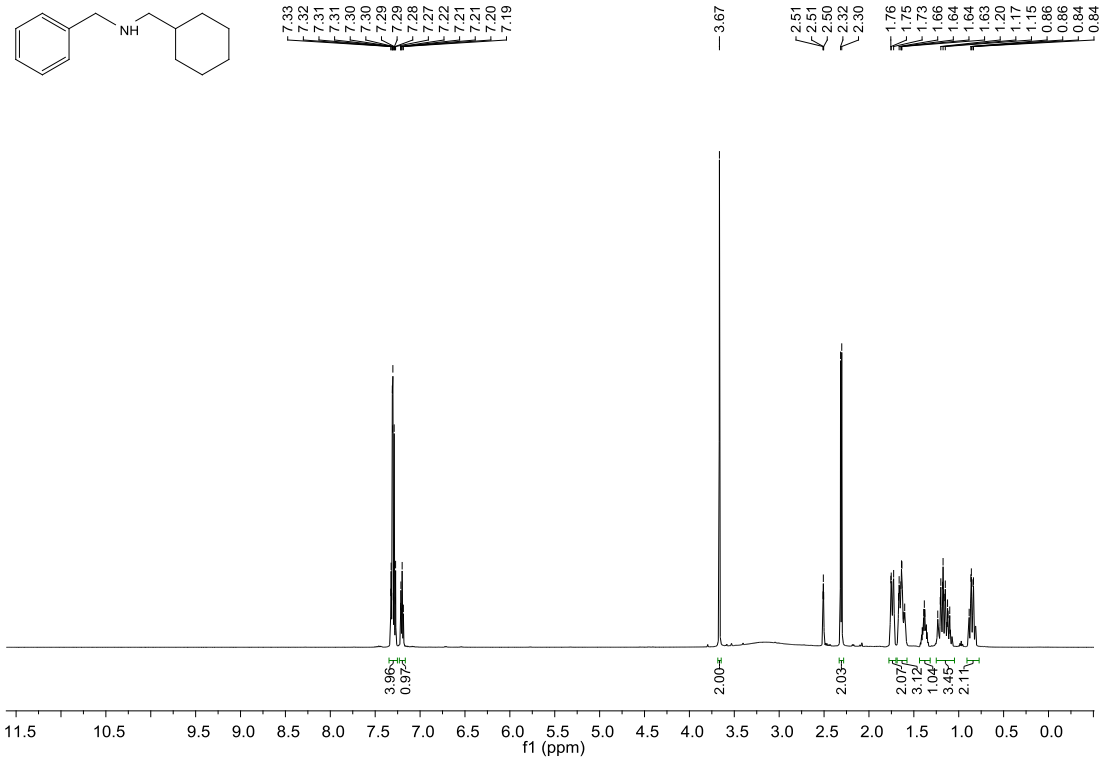


Figure S49. ^{1}H NMR (500 MHz) spectrum of **4j** in DMSO-*d*6

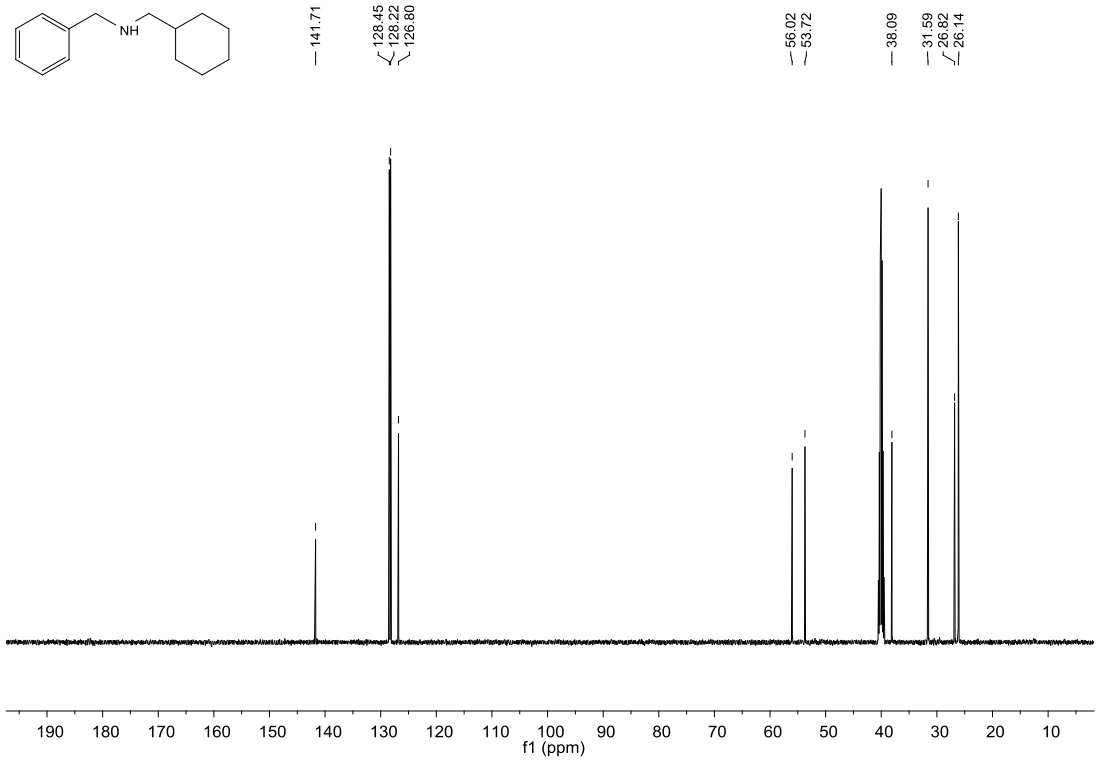


Figure S50 ^{13}C NMR (125 MHz) spectrum of **4j** in DMSO-*d*6

N-benzyl-2,2-dimethylpropan-1-amine (4k)

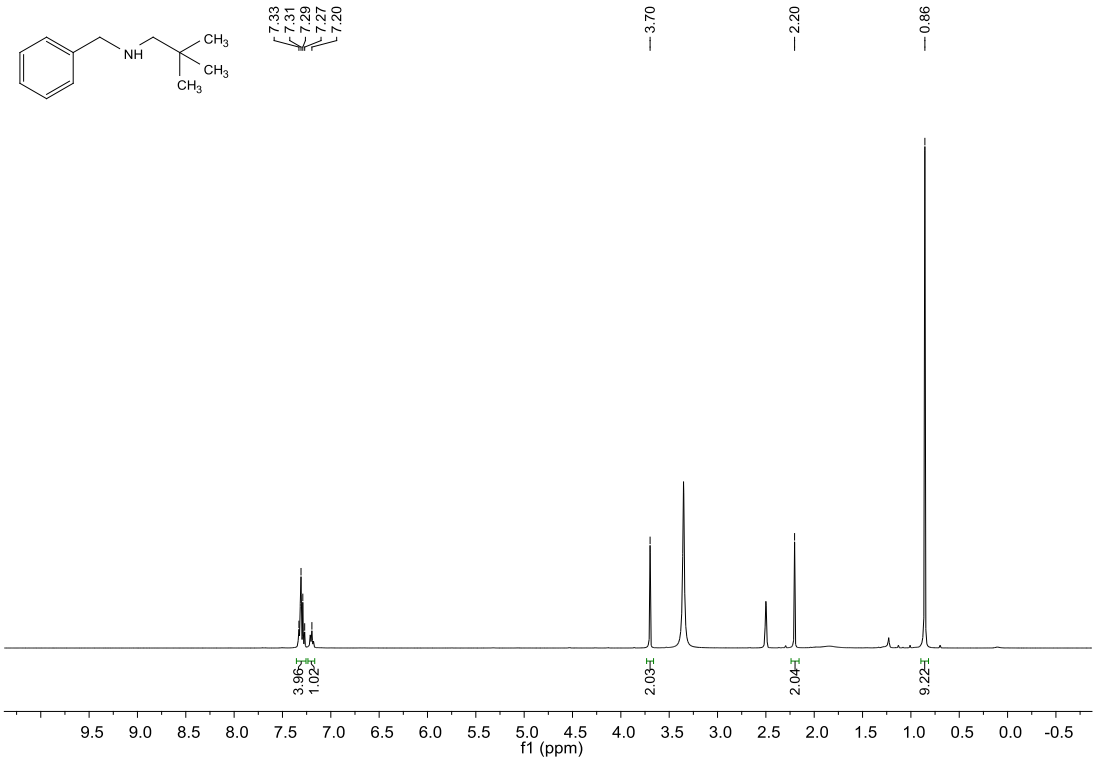


Figure S51. ^{1}H NMR (400 MHz) spectrum of **4k** in DMSO-*d*6

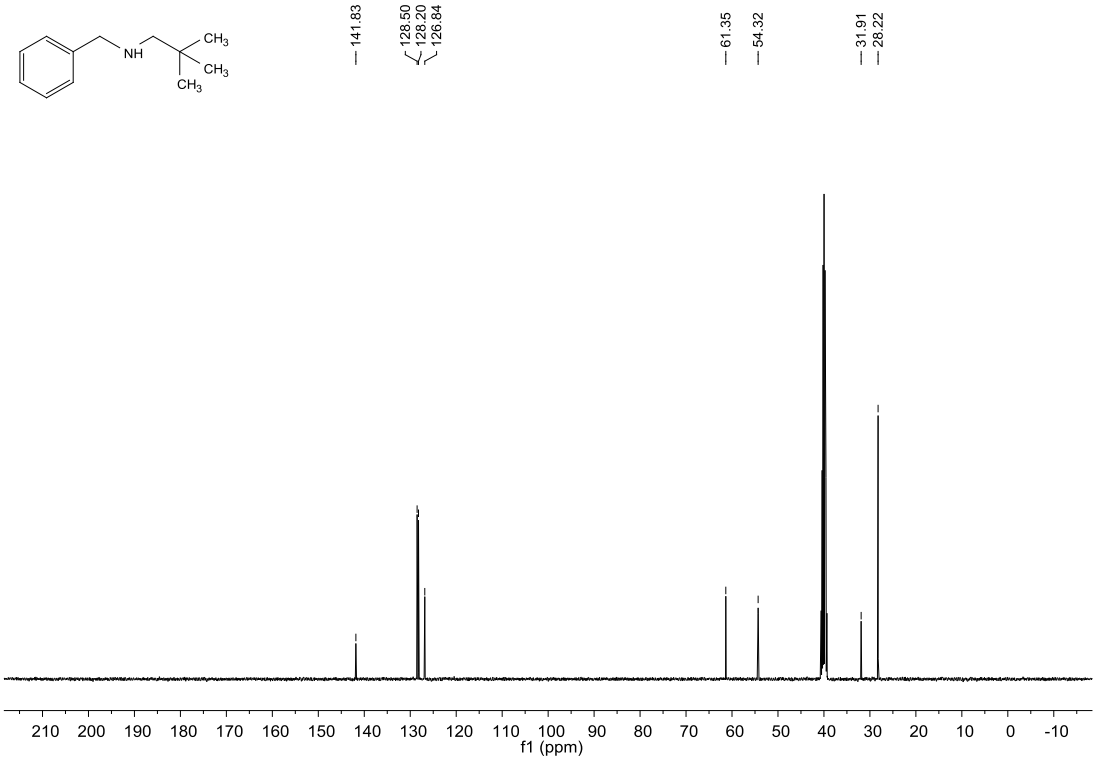


Figure S52 ^{13}C NMR (100 MHz) spectrum of **4k** in DMSO-*d*6

N-phenethylpropan-1-amine (4l)

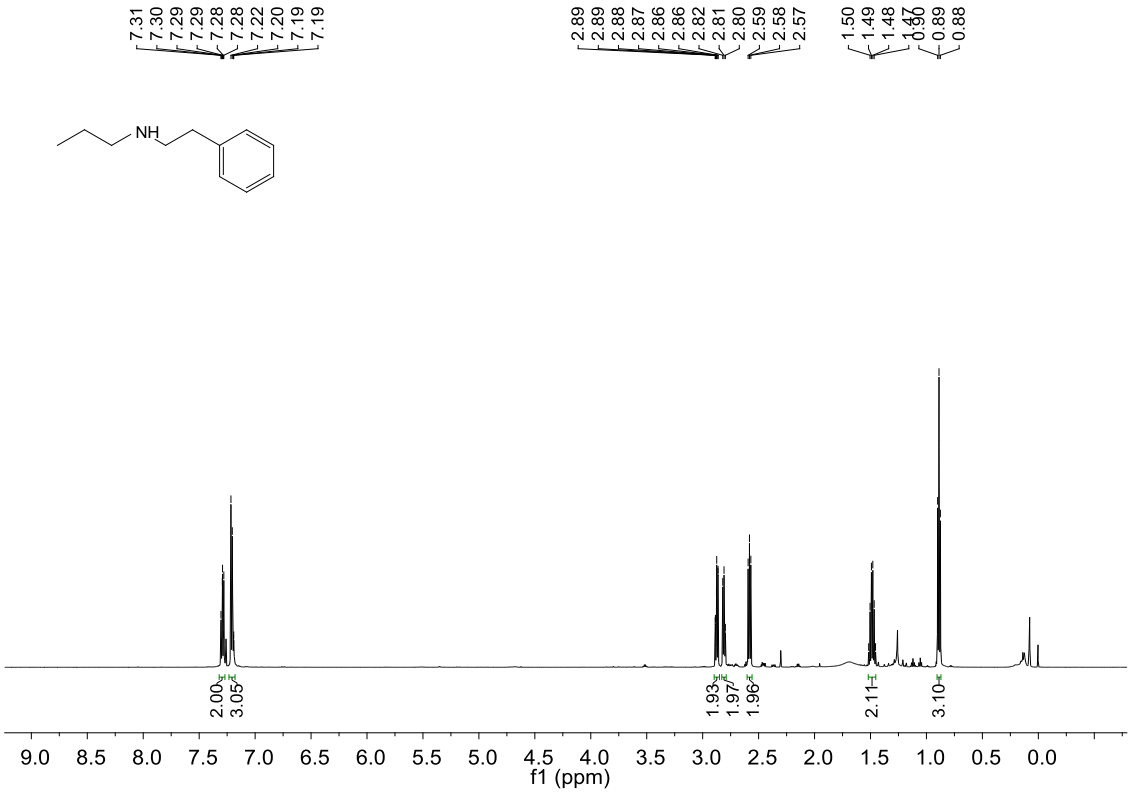


Figure S53. ^{1}H NMR (600 MHz) spectrum of **4l** in $CDCl_3$

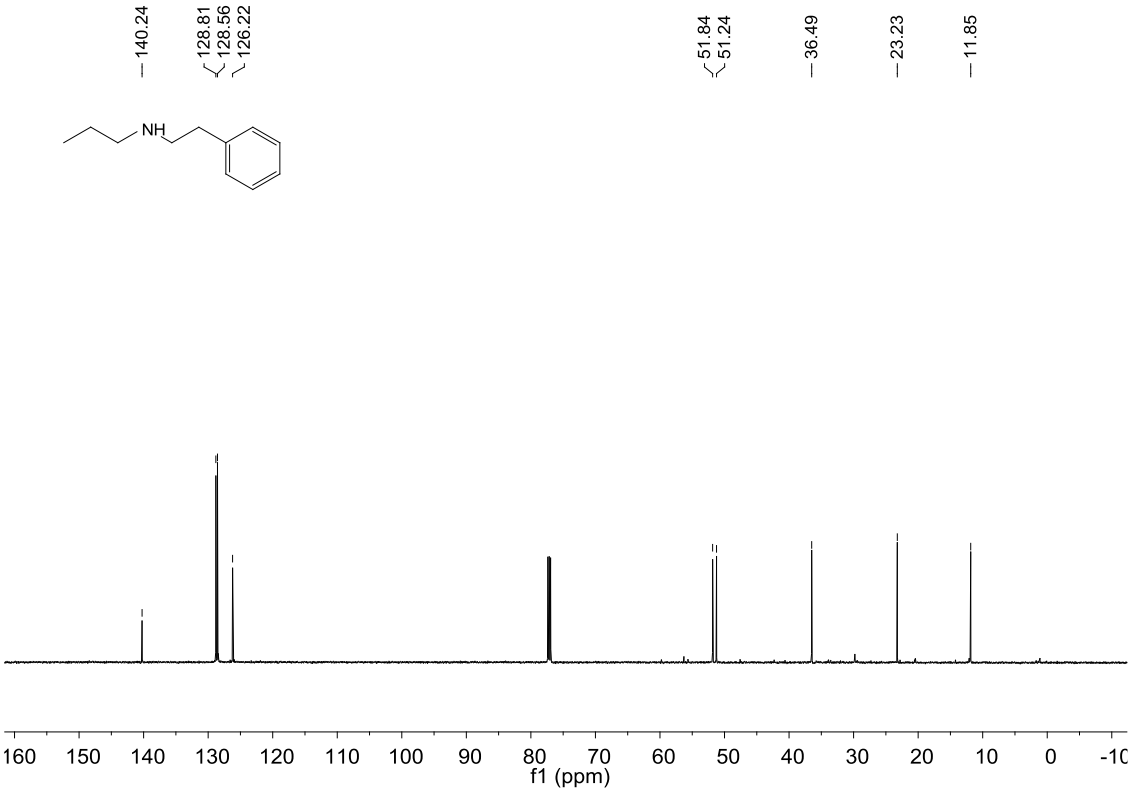


Figure S54 ^{13}C NMR (150 MHz) spectrum of **4l** in $CDCl_3$

N-ethyl-1-phenylethan-1-amine (4m)

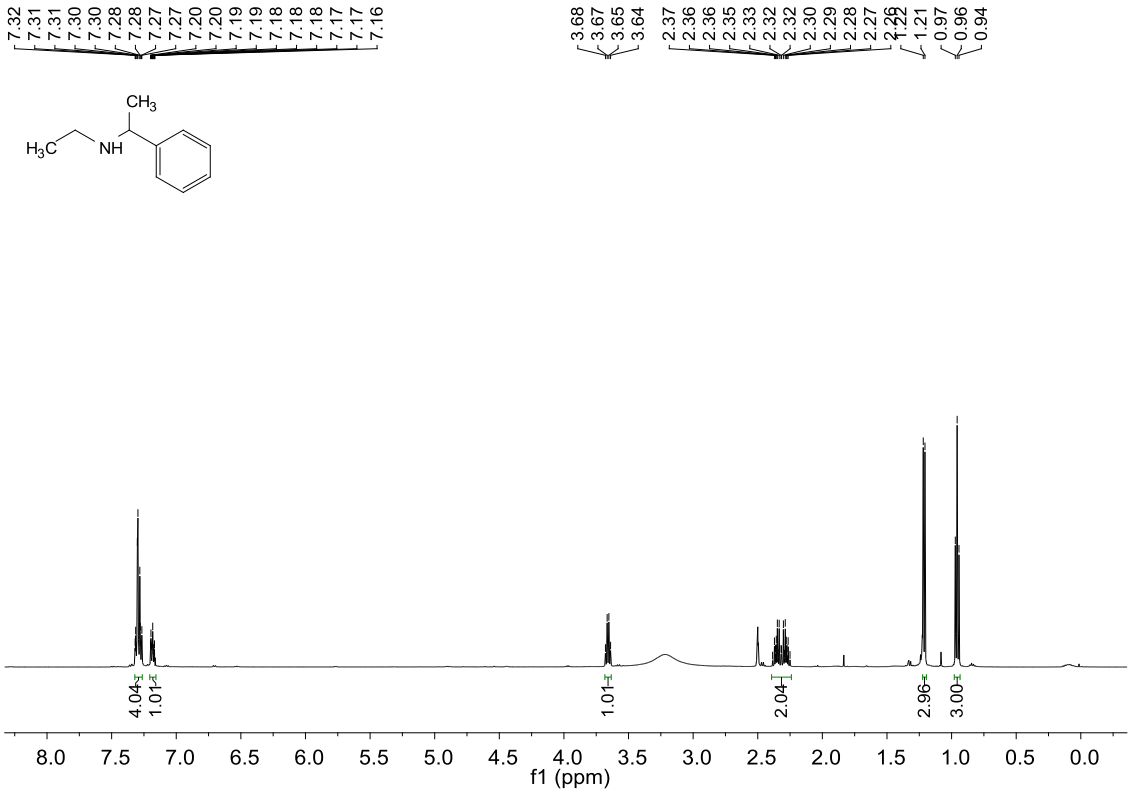


Figure S55. ^{1}H NMR (500 MHz) spectrum of **4m** in DMSO-*d*6

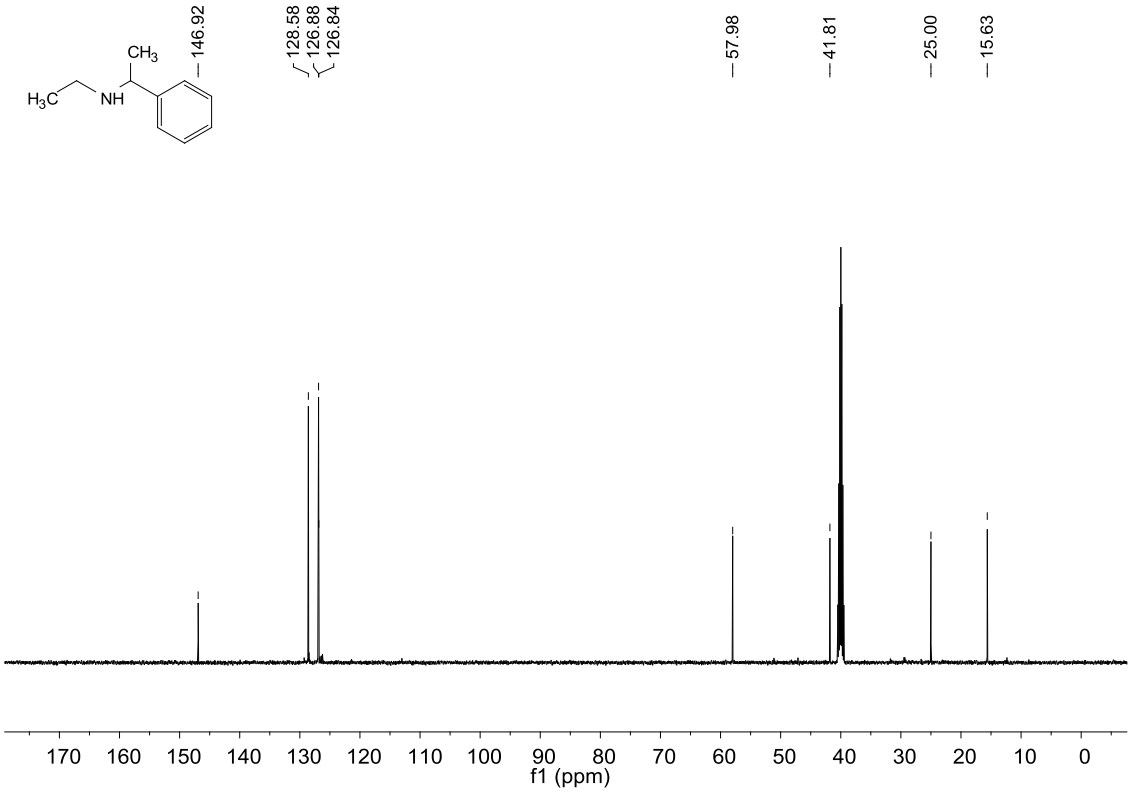


Figure S56 ^{13}C NMR (125 MHz) spectrum of **4m** in DMSO-*d*6

N-(cyclohexylmethyl)hexan-1-amine (4n)

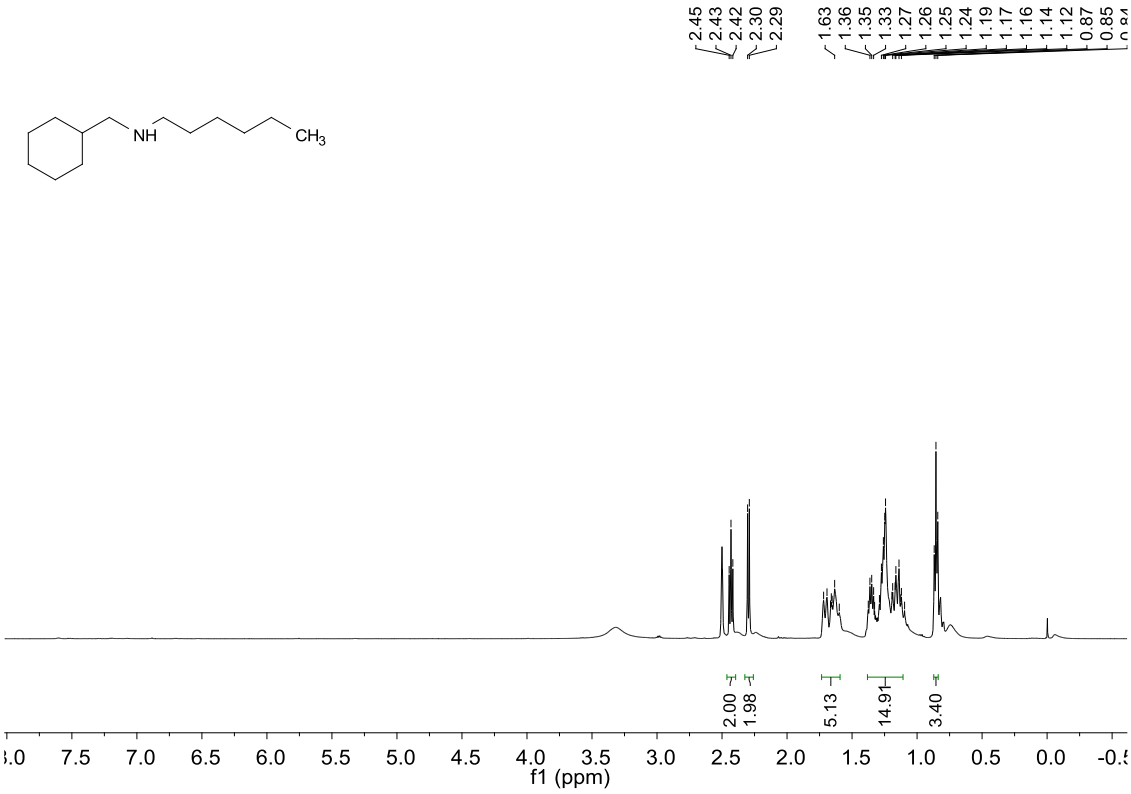


Figure S57. ^{1}H NMR (500 MHz) spectrum of **4n** in DMSO-*d*6

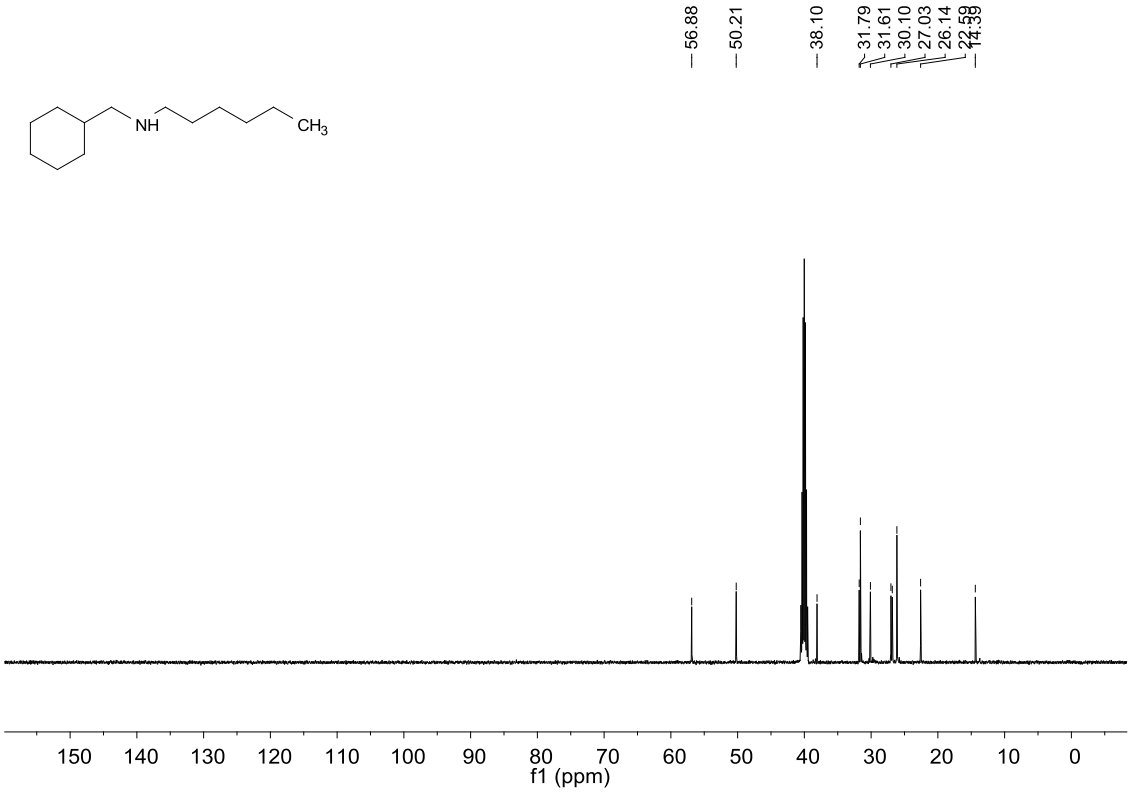


Figure S58 ^{13}C NMR (125 MHz) spectrum of **4n** in DMSO-*d*6

N-hexylcyclohexanamine (4o)

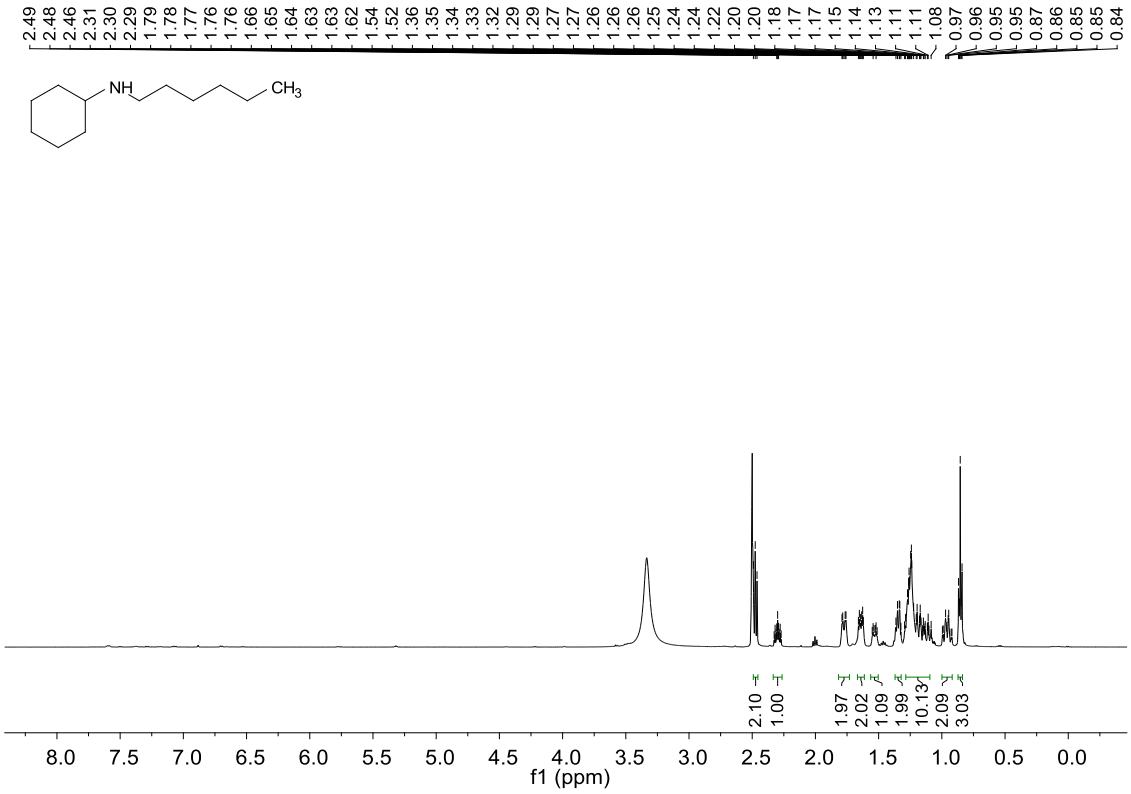


Figure S59. ^{1}H NMR (500 MHz) spectrum of **4o** in DMSO-*d*6

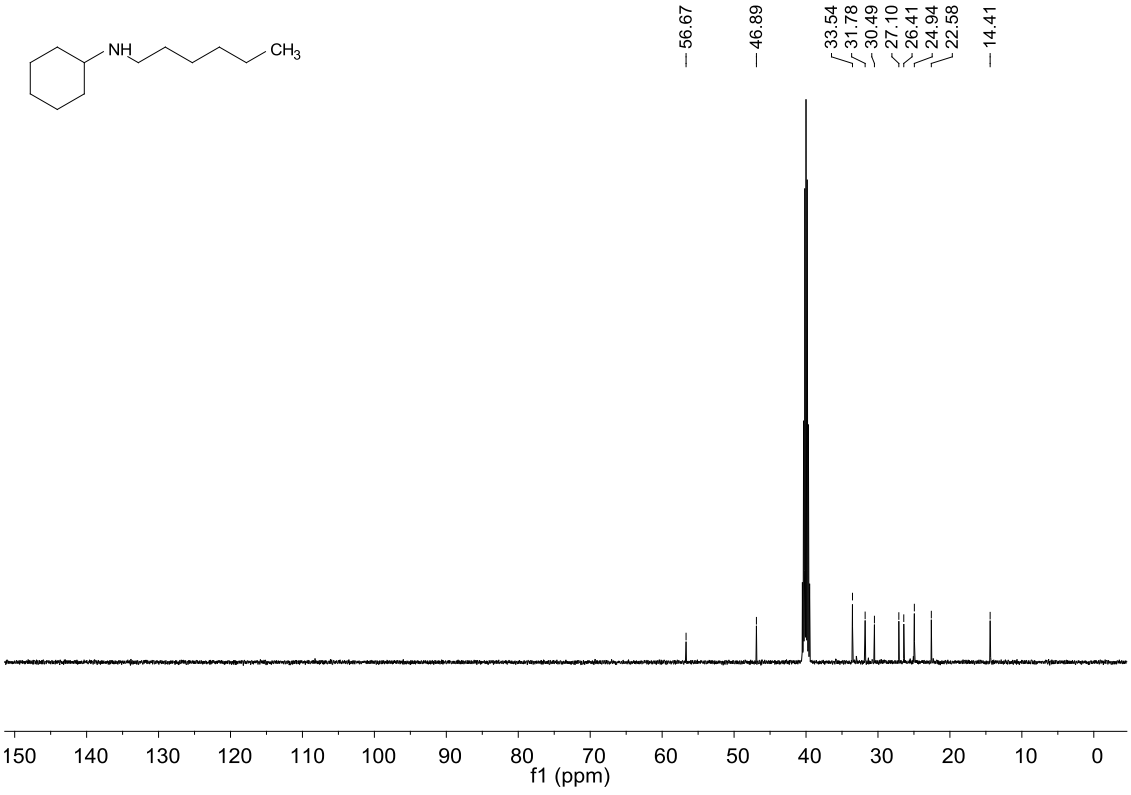


Figure S61 ^{13}C NMR (125 MHz) spectrum of 4o in DMSO-*d*6

N-methylaniline (4p)

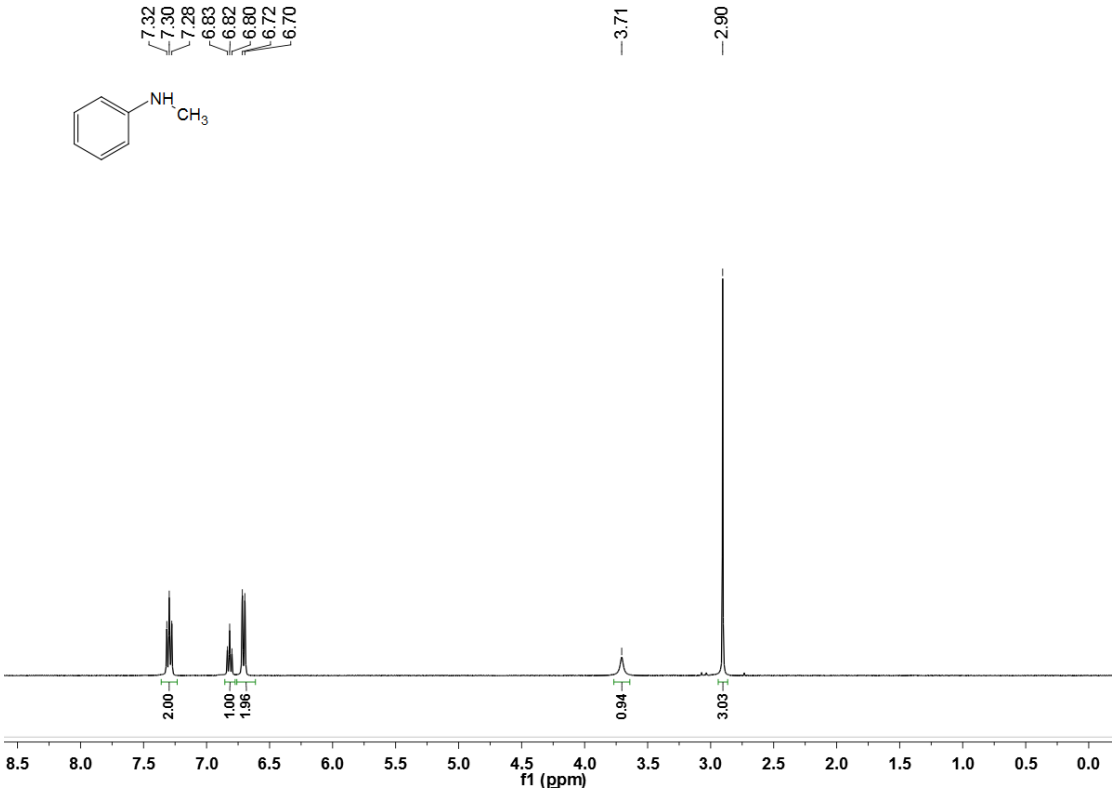


Figure S61. ^{1}H NMR (400 MHz) spectrum of **4p** in $CDCl_3$

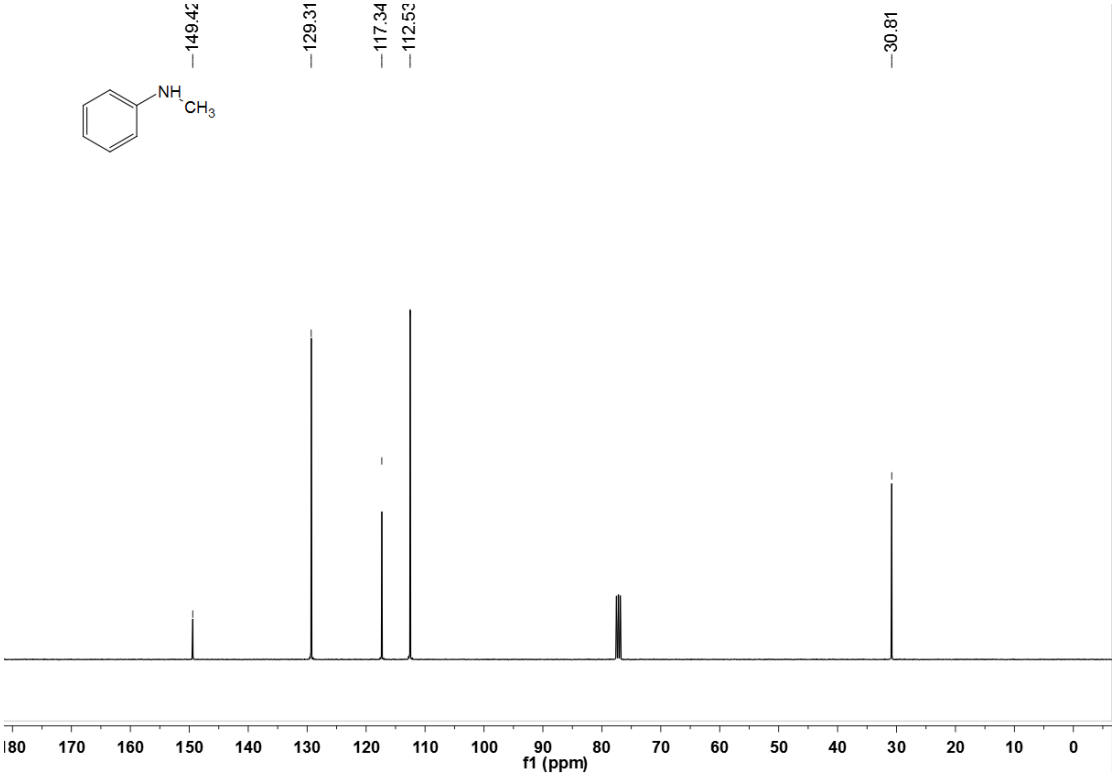


Figure S62 ^{13}C NMR (100 MHz) spectrum of **4p** in $CDCl_3$

N-methylcyclohexanamine (4q)

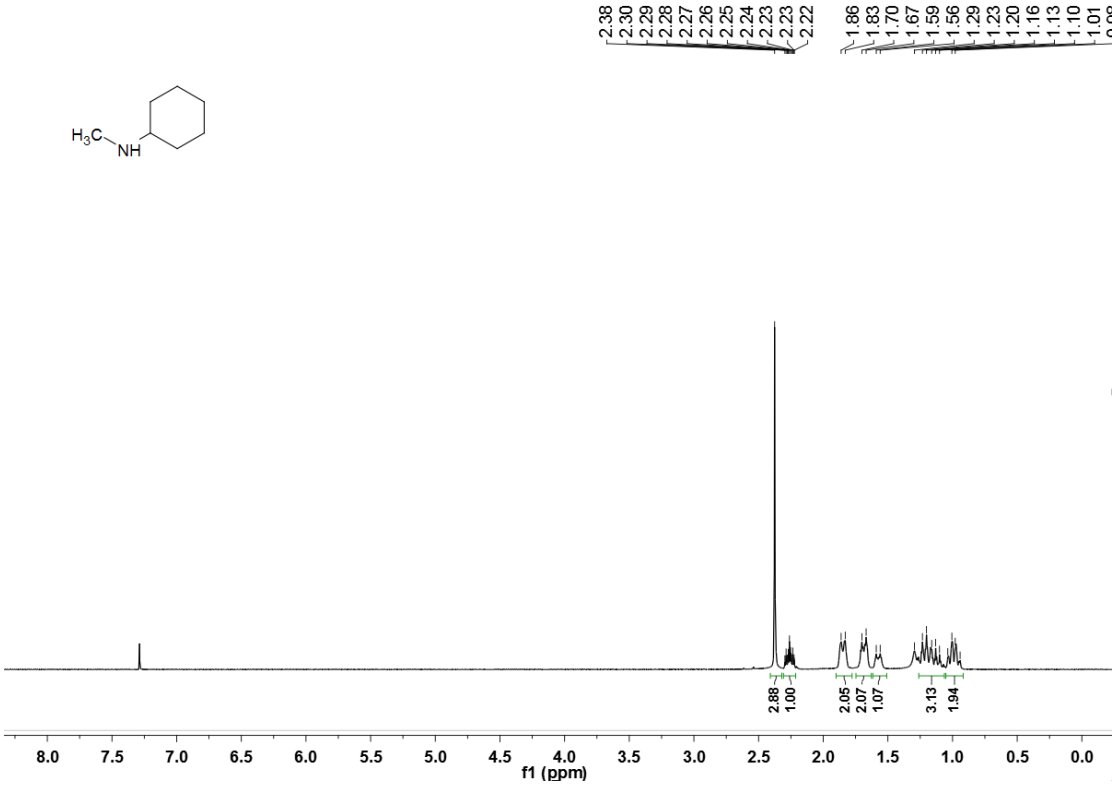


Figure S63. ^{1}H NMR (400 MHz) spectrum of **4q** in $CDCl_3$

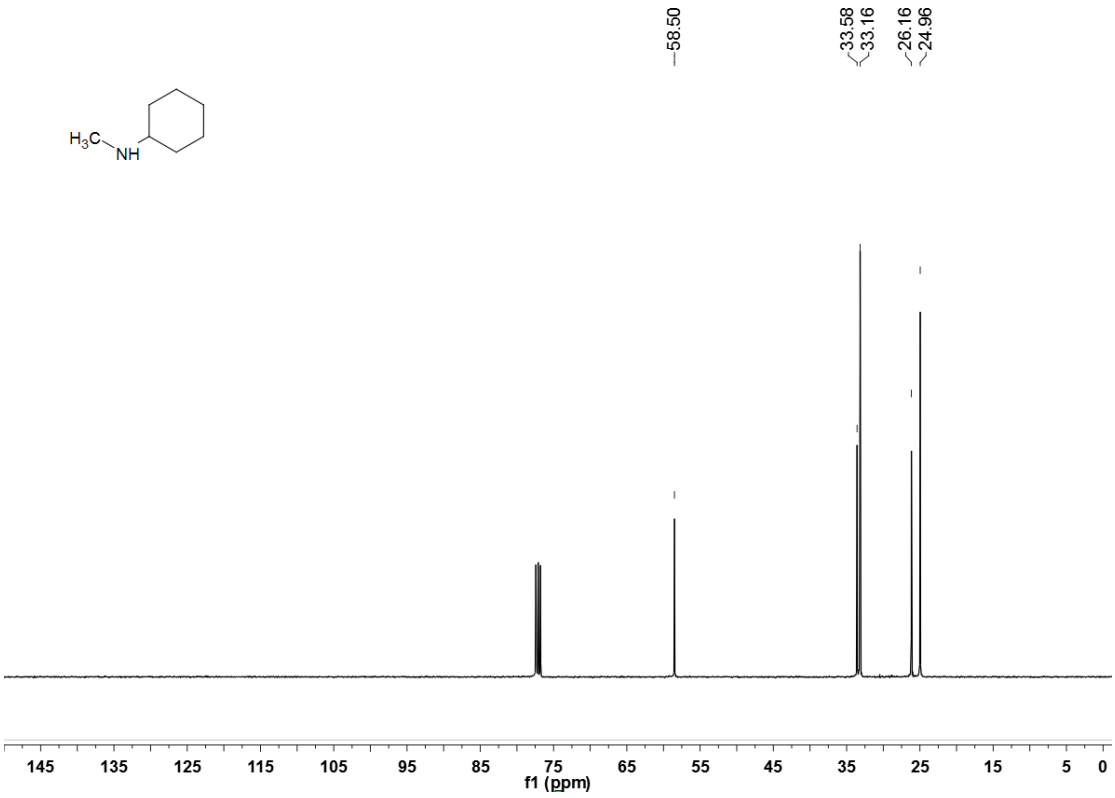


Figure S64 ^{13}C NMR (100 MHz) spectrum of **4q** in $CDCl_3$

1,2,3,4-tetrahydroquinoline (6b)

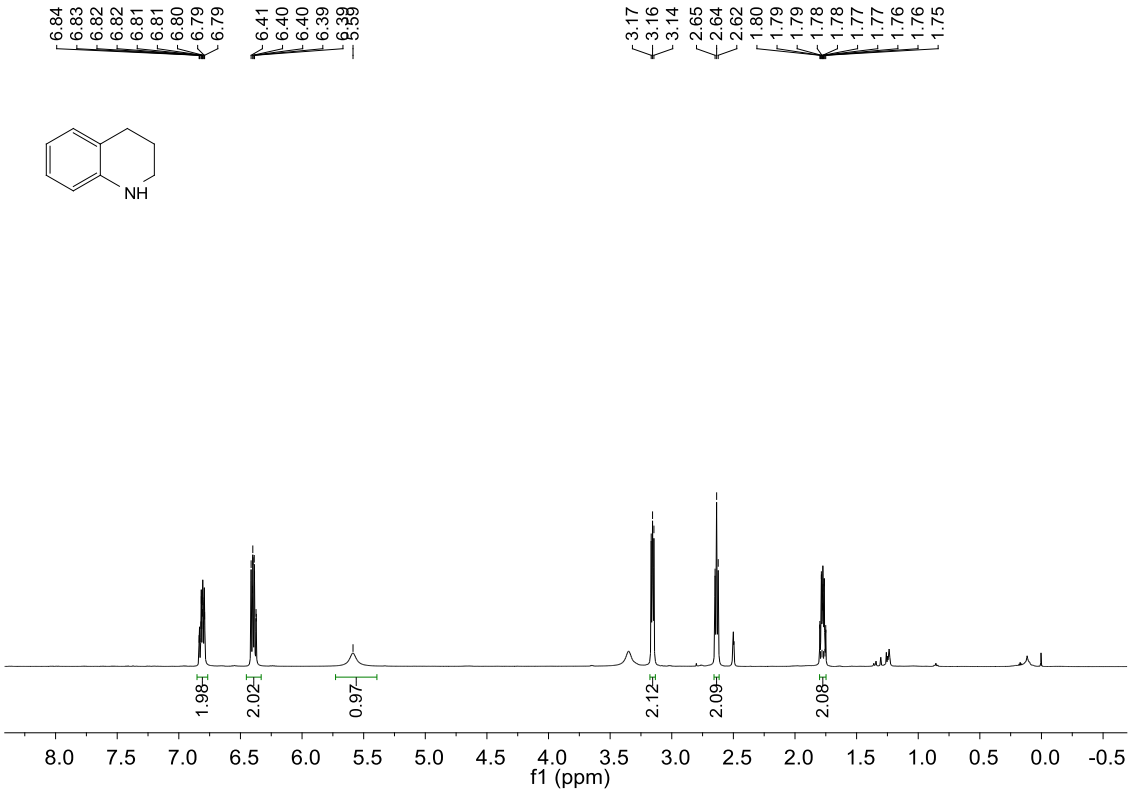


Figure S65. ^{1}H NMR (500 MHz) spectrum of **6b** in DMSO-*d*6

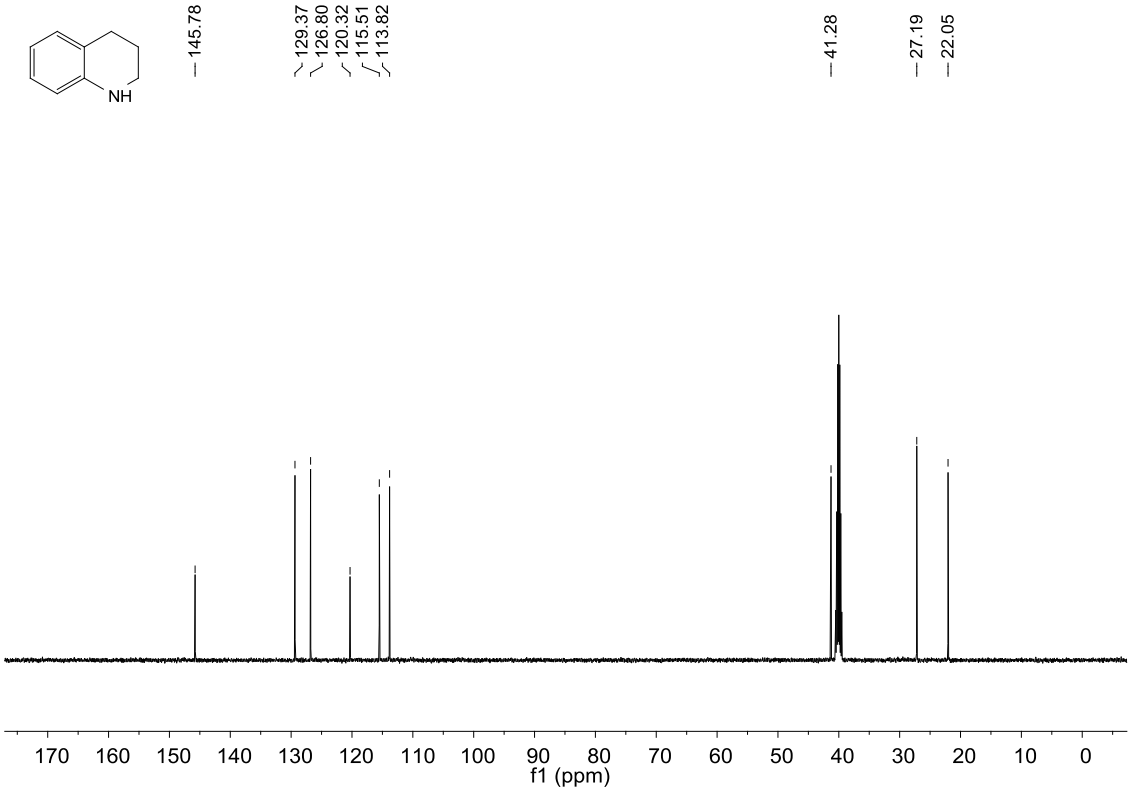


Figure S66 ^{13}C NMR (125 MHz) spectrum of **6b** in DMSO-*d*6

2,3,4,5-tetrahydro-1H-benzo[b]azepine (6d)

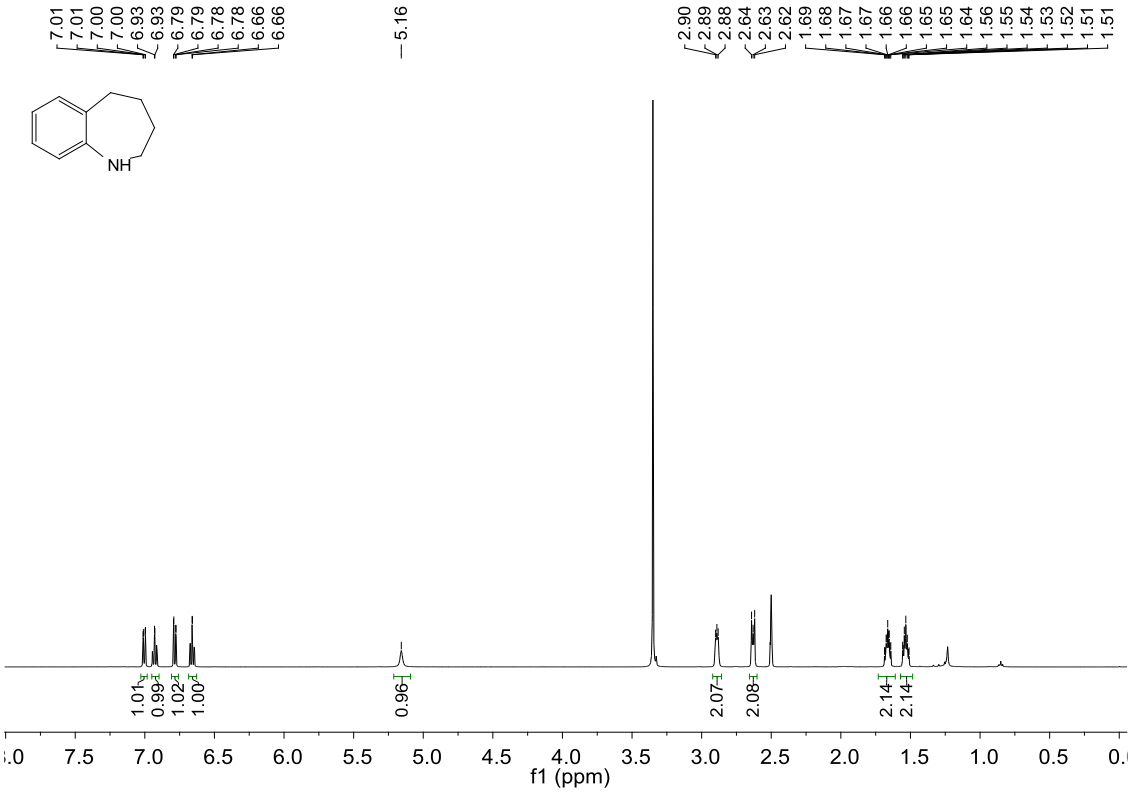


Figure S67. ^{1}H NMR (500 MHz) spectrum of **6d** in DMSO-*d*6

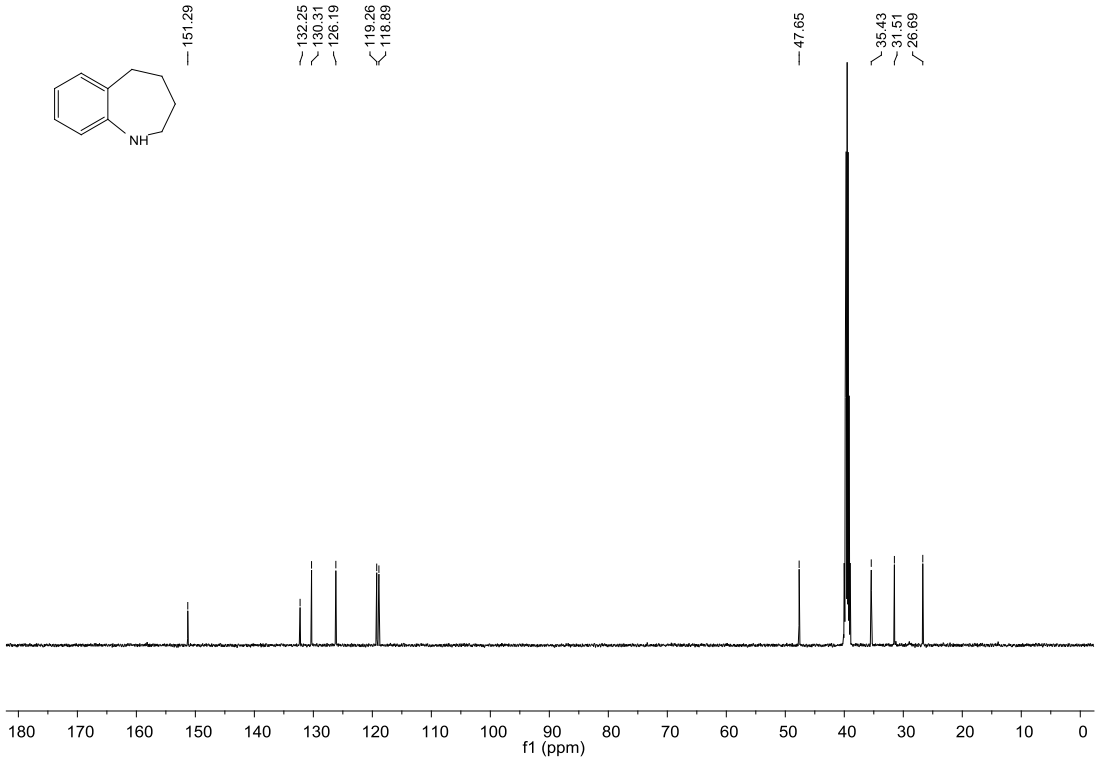


Figure S68 ^{13}C NMR (125 MHz) spectrum of **6d** in DMSO-*d*6

Azacyclotridecane (6e)

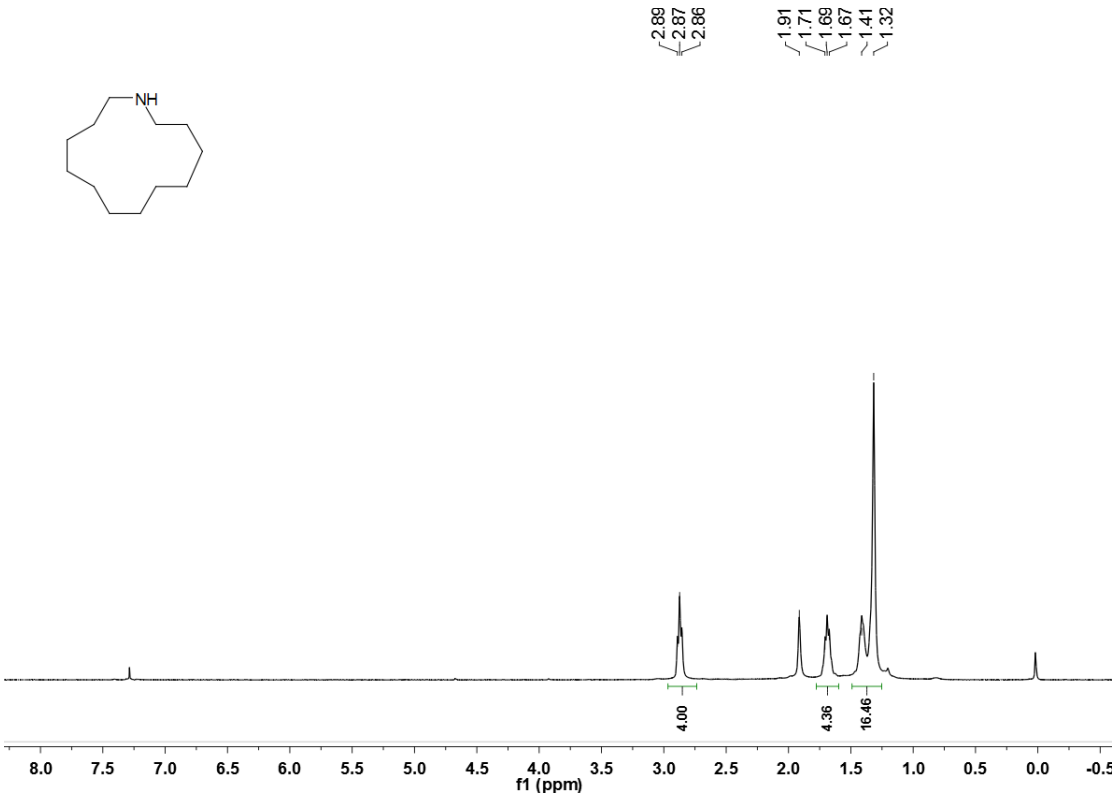


Figure S69. ^{1}H NMR (400 MHz) spectrum of **6e** in $CDCl_3$

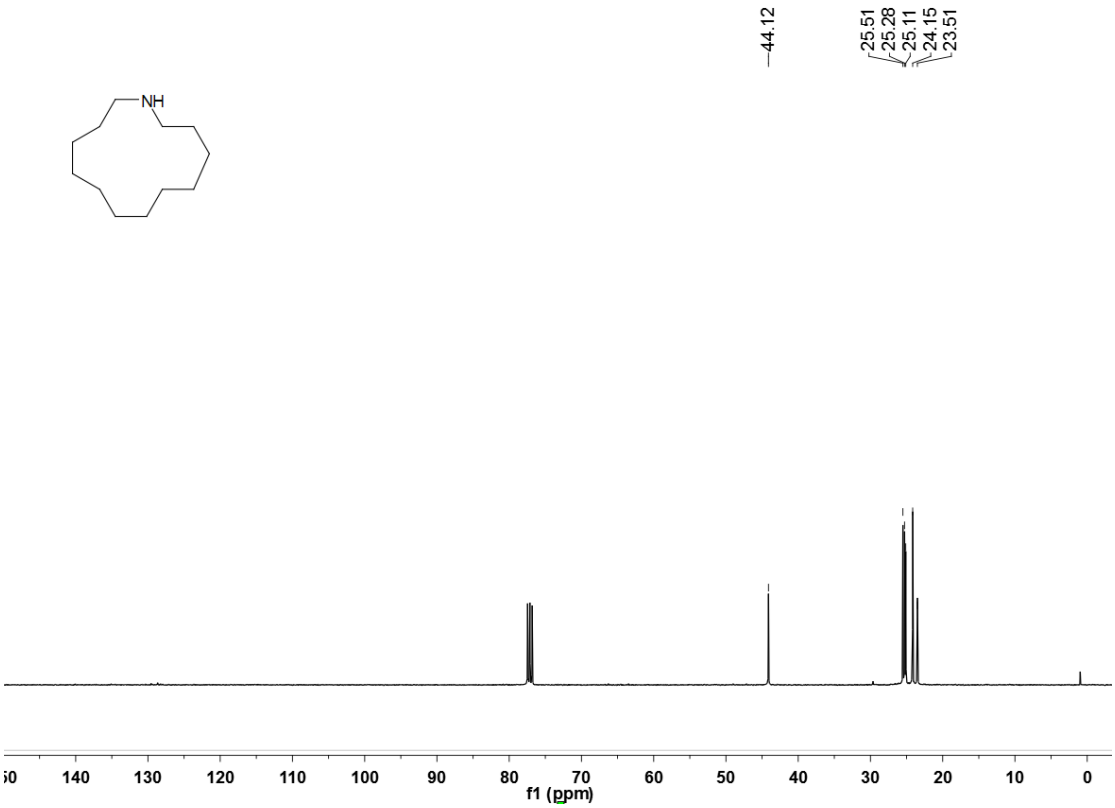


Figure S70 ^{13}C NMR (100 MHz) spectrum of **6e** in $CDCl_3$

6. References

1. Y. Pan, Z. Luo, J. Han, X. Xu, C. Chen, H. Zhao, L. Xu, Q. Fan and J. Xiao, B(C6F5)3-Catalyzed Deoxygenative Reduction of Amides to Amines with Ammonia Borane, *Advanced Synthesis & Catalysis*, 2019, **361**, 2301-2308.
2. Z. Luo, Y. Pan, Z. Yao, J. Yang, X. Zhang, X. Liu, L. Xu and Q.-H. Fan, BF3·Et2O as a metal-free catalyst for direct reductive amination of aldehydes with amines using formic acid as a reductant, *Green Chemistry*, 2021, **23**, 5205-5211.
3. I. Chatterjee and M. Oestreich, B(C6F5)3-catalyzed transfer hydrogenation of imines and related heteroarenes using cyclohexa-1,4-dienes as a dihydrogen source, *Angew Chem Int Ed Engl*, 2015, **54**, 1965-1968.
4. J. Zhang and S. Chang, cine-Silylative Ring-Opening of alpha-Methyl Azacycles Enabled by the Silylium-Induced C-N Bond Cleavage, *J Am Chem Soc*, 2020, **142**, 12585-12590.
5. J. H. Cho, S. Byun, A. Cho and B. M. Kim, One-pot, chemoselective synthesis of secondary amines from aryl nitriles using a PdPt–Fe3O4 nanoparticle catalyst, *Catalysis Science & Technology*, 2020, **10**, 4201-4209.
6. F. I. McGonagle, D. S. MacMillan, J. Murray, H. F. Sneddon, C. Jamieson and A. J. B. Watson, Development of a solvent selection guide for aldehyde-based direct reductive amination processes, *Green Chemistry*, 2013, **15**.
7. A. Lator, Q. G. Gaillard, D. S. Merel, J. F. Lohier, S. Gaillard, A. Poater and J. L. Renaud, Room-Temperature Chemoselective Reductive Alkylation of Amines Catalyzed by a Well-Defined Iron(II) Complex Using Hydrogen, *J Org Chem*, 2019, **84**, 6813-6829.
8. D. Hollmann, A. Tillack, D. Michalik, R. Jackstell and M. Beller, An improved ruthenium catalyst for the environmentally benign amination of primary and secondary alcohols, *Chem Asian J*, 2007, **2**, 403-410.
9. J.-S. Ouyang, S. Liu, B. Pan, Y. Zhang, H. Liang, B. Chen, X. He, W. T. K. Chan, A. S. C. Chan, T.-Y. Sun, Y.-D. Wu and L. Qiu, A Bulky and Electron-Rich N-Heterocyclic Carbene–Palladium Complex (SIPr)Ph2od(cin)Cl: Highly Efficient and Versatile for the Buchwald–Hartwig Amination of (Hetero)aryl Chlorides with (Hetero)aryl Amines at Room Temperature, *ACS Catalysis*, 2021, **11**, 9252-9261.
10. S. B. Otvos and C. O. Kappe, Continuous-Flow Amide and Ester Reductions Using Neat Borane Dimethylsulfide Complex, *ChemSusChem*, 2020, **13**, 1800-1807.
11. T. Lebleu, J. Maddaluno and J. Legros, Selective monoalkylation of amines with light electrophiles using a flow microreactor system, *Organic Chemistry Frontiers*, 2015, **2**, 324-327.
12. A. Chartoire, A. Boreux, A. R. Martin and S. P. Nolan, Solvent-free aryl amination catalysed by [Pd(NHC)] complexes, *RSC Advances*, 2013, **3**.
13. O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. Williams, Iridium-catalysed amine alkylation with alcohols in water, *Chem Commun (Camb)*, 2010, **46**, 1541-1543.
14. X. Jv, S. Sun, Q. Zhang, M. Du, L. Wang and B. Wang, Efficient and Mild Reductive Amination of Carbonyl Compounds Catalyzed by Dual-Function Palladium Nanoparticles, *ACS Sustainable Chemistry & Engineering*, 2019, **8**, 1618-1626.
15. X. Guo and O. S. Wenger, Reductive Amination by Photoredox Catalysis and Polarity-Matched Hydrogen Atom Transfer, *Angew Chem Int Ed Engl*, 2018, **57**, 2469-2473.

16. B. Chatterjee, D. Kalsi, A. Kaithal, A. Bordet, W. Leitner and C. Gunanathan, One-pot dual catalysis for the hydrogenation of heteroarenes and arenes, *Catalysis Science & Technology*, 2020, **10**, 5163-5170.
17. R. Kokane, Y. Corre, E. Kemnitz, M. K. Dongare, F. Agbossou-Niedercorn, C. Michon and S. B. Umbarkar, Palladium supported on magnesium hydroxyl fluoride: an effective acid catalyst for the hydrogenation of imines and N-heterocycles, *New Journal of Chemistry*, 2021, **45**, 19572-19583.
18. H. Fang, G. Wang and M. Oestreich, Mild reductive rearrangement of oximes and oxime ethers to secondary amines with hydrosilanes catalyzed by B(C6F5)3, *Organic Chemistry Frontiers*, 2021, **8**, 3280-3285.